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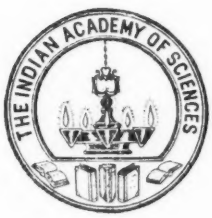

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DISPERSION OF ACOUSTIC VELOCITY IN LIQUIDS.

By B. V. Raghavendra Rao.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In view of the rapid development of research on high-frequency acoustic waves, it appears desirable to designate the portion of the acoustic spectrum having a frequency higher than a thousand mega-cycles per second as the 'hyper-sonic' region, while the 'ultra-sonic' region may be taken to extend from one to a thousand mega-cycles per second.

The presence of such high-frequency acoustic waves associated with the spontaneous thermal agitation in liquids has been definitely established by interferometric examinations of the fine structure of monochromatic radiations scattered by various liquids. The frequencies involved will necessarily depend upon the angle of scattering increasing from a thousand to six thousand mega-cycles per second as the angle of scattering is varied from about 10° to 180° (λ 4000 Å CCl_4). This is calculated from the formula

$$\lambda = 2\mu\lambda^* \sin \theta/2,$$

where λ is the wave-length of the incident radiation,

λ^* the wave-length of the acoustic waves responsible for the reflection,

μ the refractive index of the medium, and

θ the angle of scattering or reflection.

This formula is similar to the well-known Bragg's reflection formula with this difference that the refractive index of the liquid is taken into account in this case.

It is a significant question, whether these 'hyper-sonic' waves have the same velocity of propagation as that of the waves in the 'ultra-sonic' region (1—1000 mega-cycles per second) capable of being produced artificially in the laboratory by the piezo-electric method. The 'ultra-sonic' velocities can be measured with a high degree of precision which as yet, cannot be approached in the 'hyper-sonic' region. In the latter, the acoustic velocity has to be calculated from the observed Doppler frequency shifts of the scattered radiation, in which it is not easy to completely avoid

sources of error such as (*a*) the angular width of the scattered beam, (*b*) the intrinsic breadth of the Doppler component, and (*c*) the imperfect monochromatism of the incident radiation, especially the influence of the hyperfine structure satellites of the incident radiation. The third source of error is particularly serious if the satellites are intense and fall near the Doppler components of the scattered radiation. It can, however, be eliminated by a proper choice of the separating distance piece of the Fabry-Perot etalon employed.

The present paper deals with the velocity determinations of these ' hyper-sonic ' waves by a study of the fine structure of the radiations scattered by liquids under suitably controlled experimental conditions. A preliminary report of the significant results of this investigation has already appeared in the columns of *Nature*.[1]

2. *Experimental Technique.*

The experimental details of photographing the interference patterns of the mercury radiations scattered by liquids and their interpretation, have already been described in the previous papers of the author on the subject.[2] In this particular paper it is proposed to outline in brief, the various precautions taken to eliminate the several sources of error already mentioned, in arriving at a reliable value of the velocity of the ' hyper-sonic ' waves associated with the spontaneous thermal energy of the liquid.

The liquid under consideration is carefully distilled *in vacuo* in a dust-free condition, into the specially constructed Wood's tube so designed as to enable one to observe the light scattered backwards. It is important to secure a perfectly dust-free liquid, since the presence of any dust particles in the liquid will cause a certain amount of general scattering of the incident light, diminishing thereby the purity of the spectrum of the molecularly scattered light. Moreover, the hyperfine structure satellites will get strengthened in intensity relative to the intensity of the Doppler components, and will thus influence the positions of the Doppler components. This is particularly serious in the case of liquids like butyl alcohol where the Doppler component is relatively weak in comparison to the main undisplaced component of the scattered radiation.

Next comes the choice of the interferometer for the examination of the fine structure of the scattered radiation. By experience gained in this particular field of work, it was decided to use a Fabry-Perot etalon, which gives a more reliable indication of the correct structure of a complex line, both in respect of components and their relative intensities, than either

a Lummer and Gehrcke plate or an echelon spectroscope. Another decided advantage of the etalon over the other two of its kind is that the resolving power and the dispersion of the instrument can be adjusted to suit our particular needs, by using different distance pieces of invar metal separating the two half silvered quartz plates of the etalon.

Coming now to the source of light to be employed, a specially designed cathode-cooled, low-density, mercury-vapour lamp was used. Such a lamp gives out bright and sharp radiations free from self-reversal and with the hyperfine structure satellites much suppressed in intensity relative to the main line. These conditions are of great importance in these experiments, performed with the object of arriving at reliable measurements of frequency shifts.

It may, at first sight, appear that it would be ideal to use a structureless radiation like the Zn 4680 Å used by one of the earlier investigators[3] in this particular line of work. But further considerations show that, on account of the low atomic weight and the high temperature at which the lamp has to be maintained for its working, the main central line of this radiation is so wide (nearly twice as wide as the Hg radiation 4358 Å) that it is impossible to arrive at reliable measurements of frequency shifts suffered by this line. As an instance, Ramm finds for the velocity of ' hyper-sonic ' waves in liquid toluene, calculated from the measurements of the frequency shifts observed with the Zn 4680 Å radiation, a value of 1200 metres per second, while that calculated from the measurements of the frequency shifts observed with the 4358 Å radiation yields a value of 1350 metres per second ; the actual ' ultra-sonic ' velocity being 1320 metres per second.

It is thus evident, that it is only in the initial stages of a work of this nature, where the reality of the Doppler components has to be established beyond doubt, that there is some justification for the use of a structureless radiation like Zn 4680 Å. But it cannot be used in an experiment wherein reliable data of the velocity of ' hyper-sonic ' waves in liquids have to be calculated from the measured frequency shifts suffered by the incident radiation after scattering.

The three mercury radiations λλ 4046 Å, 4078 Å and 4358 Å of the low-density, cathode-cooled, mercury-vapour lamp are best suited for this purpose. For, we can, by a proper choice of the distance piece separating the two plates of the etalon, get at least one of the Doppler components appearing in a region of the interference pattern, free from the influence of neighbouring hyperfine structure satellites of the incident radiation. Amongst the three mercury radiations, λ 4078 Å radiation is, in spite of its feeble

intensity, best suited because, the hyperfine structure satellites of this line are very faint in comparison with the central line. Moreover the presence of the hyperfine structure satellites is not altogether an evil, as it enables us to check up the reliability of the measurements of Doppler shifts ; almost all the important mercury radiations have been completely analysed by Schüler[4] and others.

As a test case, the interference pattern of the λ 4078 Å radiation of the low-density, cathode-cooled, mercuty-vapour lamp photographed with a 4·5 mm. gap etalon was measured and the wave-lengths of the satellites $+0{\cdot}273$ cm.$^{-1}$ and $+0{\cdot}464$ cm.$^{-1}$ calculated and compared with the original values of Schüler. The agreement was found to be within $\pm 0{\cdot}005$ cm.$^{-1}$ In fact, had the same radiation been examined with different distance pieces of the etalon as has been done in the case of the measurements of the Doppler frequency shifts, the agreement could have been brought down to as much as $\pm 0{\cdot}002$ cm.$^{-1}$ In the case of the Doppler shifts, the error in measurement has been taken to be as great as $0{\cdot}010$ cm.$^{-1}$, *i.e.*, nearly four times the error usually allowed, so as to be on the safer side while drawing conclusions on the values of the velocities of acoustic waves in liquids, calculated from the measured Doppler shifts.

Another precaution taken while measuring the interference patterns of the scattered radiations was that a positive contact print of the negative was made on to an ordinary lantern plate, so as to remove the grains of the original plate and also to facilitate placing the dark cross-hair of the micrometer eye-piece, exactly in the centre of the Doppler component which appears on the positive as a bright line. Readings were taken by different persons so as to eliminate the personal equation in measurement, and different magnifications of the micrometer eye-piece were employed and from a number of such readings the most reliable value of the Doppler frequency shifts corresponding to those Doppler components appearing in a region of the inteference pattern free from neighbouring hyperfine structure satellites, was calculated. In spite of taking all these precautions, a large margin of allowable error, *i.e.*, $\pm 0{\cdot}010$ cm.$^{-1}$ has been taken into consideration.

In the first two papers,[2] of the author entitled "*Examination of Molecularly Scattered Light with a Fabry-Perot Etalon*," Parts I and II, measurements of the observed Doppler shifts of the three mercury radiations 4046 Å, 4078 Å and 4358 Å scattered by liquids, carbon tetrachloride, toluene and benzene were given together with the calculated Doppler shifts taking into account the 'ultra-sonic' velocity data then available. More-

over, the importance of the influence of neighbouring hyperfine structure satellites on the observed Doppler shifts had not been fully realised and the mean of the two Doppler shifts was usually taken to be very near the correct value. In spite of this, it is found that the observed Doppler frequency shift in the case of carbon tetrachloride is far greater than the value calculated from the observed ' ultra-sonic ' velocity, while the observed Doppler frequency shifts previously recorded in the case of benzene and toluene agree fairly well with the values calculated from the recent ' ultra-sonic ' velocities in those liquids. The reason is not far to seek. In the case of carbon tetrachloride one of the Doppler components falls in a region of the interference pattern free from hyperfine structure satellites of the incident radiation, while in the case of benzene and toluene which have very nearly the same ' ultra-sonic ' velocities, neither of the two Doppler components fall in a region free from the satellites (5 mm. being the distance piece separating the plates of the etalon). In addition to this, the high anisotropy of the molecules of liquids benzene and toluene, resulted in the appearance of a continuous beckground overlapping the discrete lines of the interference pattern of the scattered radiation in distinct contrast to the clear and sharp patterns obtained with the radiations scattered by liquid carbon tetrachloride. From the foregoing it is clear that liquids like benzene and toluene are not ideal for the study of the dispersion of acoustic velocity in liquids in the ' hyper-sonic ' region. A search was then made for a liquid which could exhibit a Doppler shifted component camparable in intensity with that shown by liquid toluene but without the continuous background accompanying the scattered radiation. Liquid acetone was found to satisfy the above conditions and this paper deals with the ' hyper-sonic ' velocity determinations in liquids carbon tetrachloride and acetone.

3. Results.

Liquid carbon tetrachloride.—As already indicated, a 5 mm. gap Fabry-Perot etalon was found to be best suited for the study of the Doppler shifts suffered by the three mercury radiations λλ 4046 Å, 4978 Å and 4358 Å. In the case of the two radiations 4046 Å and 4358 Å, it will be found that at least one of the Doppler components falls in a region of the interference pattern of the scattered radiation free from the influence of close hyperfine structure satellites. In the case of λ 4078 Å radiation, however, the hyperfine structure satellites are so faint relative to the main line that their presence in the vicinity of the Doppler components will not sensibly affect the measurements of the frequency shifts. This can easily be seen from the table containing the measured Doppler shifts given below ;—

TABLE I.

Liquid carbon tetrachloride:—*5 mm. F-P etalon. Angle of scattering* 180°.

Radiation	Observed Doppler shift	Calculated Velocity in m./sec.	'Ultra-sonic' Velocity in m./sec.
λ 4046 Å	+ 0·285 cm.$^{-1}$ *− 0·261* „	1070 ± 25	928 ± 1
λ 4078 Å	+ 0·261 „ − 0·259 „	1074 ± 25	928 ± 1
λ 4358 Å	*+ 0·240* „ − 0·236 „	1068 ± 25	928 ± 1

In the case of λ 4046 Å radiation, the Doppler component (+ 0·285 cm.$^{-1}$) is in the midst of a group of unresolved hyperfine structure satellites and is hence shifted away from the centre by the influence of the strongest satellite of that group, *i.e.*, (+ 0·330 cm.$^{-1}$). On the other hand, the other Doppler component (− 0·261 cm.$^{-1}$) falls in a region free from hyperfine structure satellites, the nearest group being the two satellites + 0·668 cm.$^{-1}$ and − 0·394 cm.$^{-1}$ which are close to one another and clearly resolved from the neighbouring Doppler component (− 0·261 cm.$^{-1}$). This is clear from the photographic reproductions of the interference patterns of the scattered and incident λ 4046 Å radiations given in Plate III. And for these reasons, the measured value of the (− 0·261 cm.$^{-1}$) Doppler shift is considered to be quite reliable. This value of Doppler frequency shift corresponds to a 'hypersonic' velocity of 1070 metres per second, while the actual 'ultra-sonic' velocity in carbon tetrachloride at the corresponding temperature is only 928 ± 1 metres per second.

In the case of λ 4358 Å radiation, the same considerations as above will show that the frequency shift given by the Doppler component (+ 0·240 cm.$^{-1}$) is more reliable than that of the Doppler component (− 0·236 cm.$^{-1}$) which is shifted towards the longer wave-length, due to the presence of very close hyperfine structure satellites.

Coming now to the λ 4078 Å radiation, the neighbouring hyperfine structure satellites have, on account of their relatively feeble intensity, practically no influence on the measured Doppler shifts at all as can be noticed from the close agreement between the calculated and observed values of Doppler shift + 0·261 cm.$^{-1}$ and − 0·259 cm.$^{-1}$ Hence there is

some justification for taking in this case, the mean of the two values as representing the correct Doppler shift.

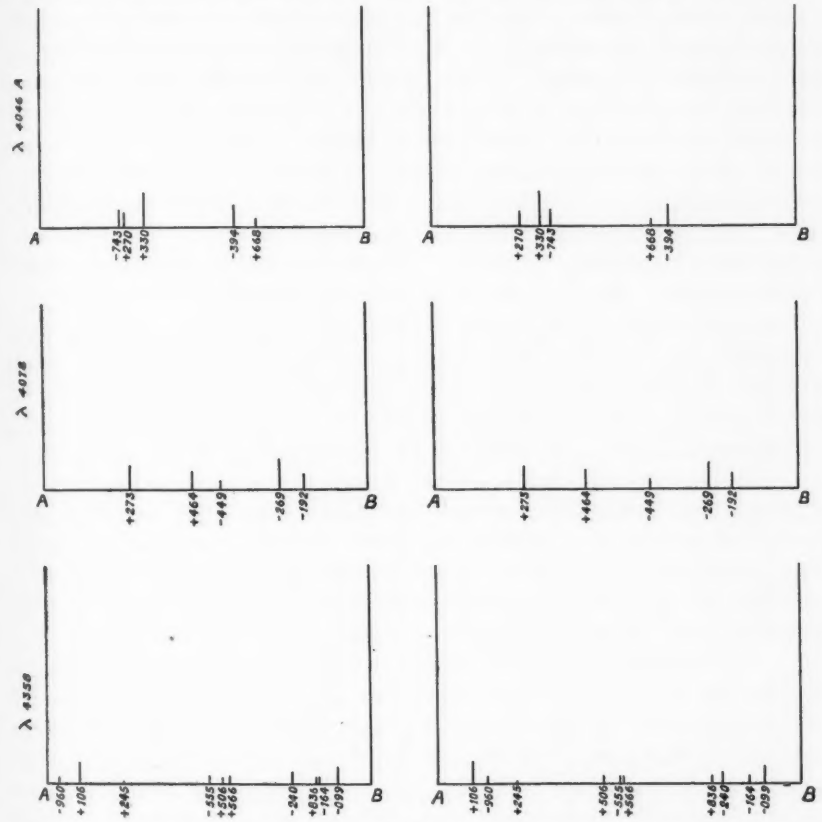

FIG. 1.

Another important point needs elucidation at this stage. That is, while trying to get a particular region of the interference pattern (where the Doppler components are expected to occur) free from hyperfine structure satellites, one should bear in mind not to make the satellites crowd up at the main lines, in which case, the main lines will become very broad similar to that in the interfernce pattern of λ 4358 Å radiation obtained with a 5 mm. gap etalon. In all such cases, it is very difficult to fix the centre of the main lines with the result that the uncertainty of centring which was

avoided in the case of the Doppler components has now crept into the main components. Either way, it is evident that no stress can be placed on all such measurements. That is exactly why the main lines and at least one of the Doppler lines have to be free from the influence of neighbouring hyperfine structure satellites. From all the above points of view, the measurements of the Doppler shifts towards the longer wave-length, suffered by the mercury λ 4046 Å radiation photographed with a 5 mm. gap etalon are most reliable. This value of $-0{\cdot}261$ cm.$^{-1}$ yields for the velocity of the 'hyper-sonic' waves in carbon tetrachloride a value of 1070 metres per second. Even allowing for the most liberal estimate of the error of measurement creeping in, *i.e.*, of the order of $\pm 0{\cdot}010$ cm.$^{-1}$ which corresponds to about ± 25 metres per second in the observed velocity, one still finds that the accepted 'ultra-sonic' velocity at the corresponding temperature is less than the 'hyper-sonic' velocity by as much as 150 metres per second.

Liquid acetone.—In the case of acetone, the invar distance piece separating the silvered plates of the etalon was 4·5 mm. thick. This was deemed necessary, as the 'ultra-sonic' velocity in acetone had been recorded as 1205 metres per second, the region of the interference pattern of λ 4046 Å between the main line and the two close hyperfine structure satellites $+0{\cdot}668$ cm.$^{-1}$ and $-0{\cdot}394$ cm.$^{-1}$ had to be as wide as possible. In the diagrammatic representation of the distribution of hyperfine structure satellites in the interference pattern of λ 4046 Å radiation corresponding to the 4·5 mm. gap etalon it will be found that the hyperfine structure satellite $+0{\cdot}668$ cm.$^{-1}$ has now come over to the other side of the satellite $-0{\cdot}394$ cm.$^{-1}$ leaving a clear gap of nearly $0{\cdot}4$ cm.$^{-1}$ between itself and the main line. In the interference pattern of the λ 4358 Å radiation, it will be noticed that but for the central group of satellites narrowing down a bit, the complication of the satellites near the main line is as bad as that with the 5 mm. gap etalon. The relative positions of the hyperfine structure satellites of the λ 4078 Å radiation is practically the same as before except that the central two satellites $+0{\cdot}464$ cm.$^{-1}$ and $-0{\cdot}449$ cm.$^{-1}$ have now moved apart by $0{\cdot}1$ cm.$^{-1}$ more than before.

We shall restrict ourselves only to the radiation λ 4046 Å. The other two radiations λ 4078 Å and λ 4358 Å were considered in detail in the case of carbon tetrachloride only with the object of clarifying certain important precautions to be taken in such problems.

In the interference pattern of the incident λ 4046 Å radiation photographed with the 4·5 mm. gap etalon, in between two successive main orders are to be seen, two discrete components. One of them is fairly intense

and wide as well, comprising as it does the three unresolved hyperfine structure satellites + 0·270 cm.$^{-1}$, + 0·330 cm.$^{-1}$ and − 0·740 cm.$^{-1}$, and the other comparatively faint and sharp component consisting of the two remaining satellites + 0·668 cm.$^{-1}$ and − 0·394 cm.$^{-1}$ On comparing this with the interference pattern of the same radiation after scattering by acetone, it will be seen that in between consecutive main orders, we have in all four components. One of the expected Doppler components, *i.e.*, the one towards the shorter wave-length, falls very near the group of the three unresolved satellites giving rise to a broad and fairly strong component, while the other Doppler component, *i.e.*, towards the longer wave-length, occurs in a region free from the influence of any of the satellites as a sharp and discrete line. Of the other two faint components of almost the same intensity in the centre, one was found on measurement to be the combination of the two hyperfine structure satellites + 0·668 cm.$^{-1}$ and − 0·394 cm.$^{-1}$ noticeable in the interference pattern of the incident line as well. The other remaining faint component was found on measurement to be at a distance of + 0·547 cm.$^{-1}$ from the centre of the main line. After a careful examination of all the possibilities, it was found that this new component was the Doppler shift corresponding to the group of hyperfine structure satellites concentrated at + 0·330 cm.$^{-1}$, since the frequency shift of this new component from its parent line (group of three satellites) is + 0·216 cm.$^{-1}$ while the corresponding frequency shift suffered by the central main line is − 0·221 cm.$^{-1}$ Moreover, the relative intensity of the new component to its parent line is very nearly the same as that of the Doppler component (− 0·221 cm.$^{-1}$) to its parent line. This point of view will be clear from a perusal of the diagrammatic representation in Fig. 2.

The new fact arising from the above regarding the fine structure of the Doppler component, similar to the fine structure of the incident line, is not surprising, but the fact that in a liquid like acetone where the Doppler scattering is so intense, it has been possible to obtain for the first time, the fine structure of the Doppler component, is worth recording. Incidentally it explains how such fine structure components of the Doppler components might have easily been mistaken for the presence of multiple Doppler components, *i.e.*, of higher order reported by Gross in his earlier communications to *Nature*.[5]

The measured Doppler shifts of the main Doppler component and its fine structure satellite from their parent radiations, are within the errors of measurements sensibly the same, *i.e.*, − 0·221 cm.$^{-1}$ and + 0·216 cm.$^{-1}$ respectively. Taking into account the value of −0·221 cm.$^{-1}$ as the more

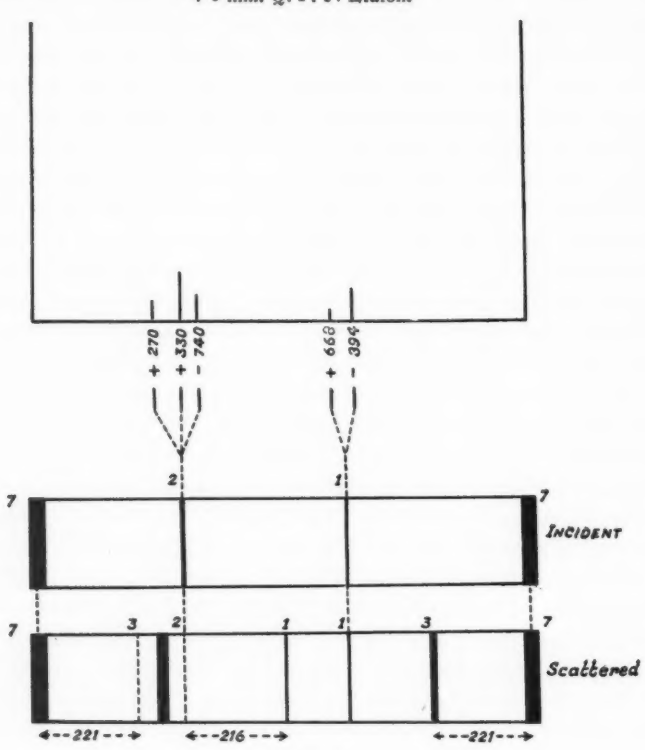

FIG. 2.

reliable one, the calculated ' hyper-sonic ' velocity in acetone comes out as 978 ± 25 metres per second while the ' ultra-sonic ' velocity at the corresponding temperature is as high as 1205 metres per second. Thus the ' hyper-sonic ' velocity is in this case less than the ' ultra-sonic ' velocity by as much as 227 ± 25 metres per second.

Liquids benzene and toluene.—In the case of these two liquids, on account of the continuous background and the appearance of the Doppler components exactly in the vicinity of the hyperfine structure satellites in the case of all the three radiations of mercury and particularly in the case λ 4046 Å, it is not possible to obtain reliable measurements of Doppler frequency shifts with as much accuracy as in the last two cases discussed above. Of there being dispersion of acoustic velocity even in these liquids between the ' hyper-sonic ' and ' ultra-sonic ' values there is no doubt, but

the exact value of the ' hyper-sonic ' velocity is not possible to be recorded with sufficient accuracy to warrant conclusions to be drawn from them.

4. Discussion.

It is hardly necessary to point out that the dispersion of acoustic velocity with frequency, is intimately connected with the anomalous damping of high frequency acoustic waves. This is particularly true in gases, where an anomalous acoustic damping has been found as a function of frequency, being a maximum very near the ' relaxation frequency ' of the molecules. At very low frequencies the experimentally observed acoustic damping agrees very well with the value calculated from the classical hydrodynamic formula, and at very high frequencies, far beyond the ' relaxation frequency ', the acoustic damping comes down from its high anomalous value to the one calculated from the classical formula. The explanation that at such high frequencies, that part of the specific heat corresponding to the excitation of the atomic vibrations which require a definite ' time of relaxation ' vanishes, with the result, that the specific heat and hence the adiabatic compressibility of the medium changes with frequency, has successfully accounted for the observed anomalous damping in gases. From the above result (*i.e.*, the adiabatic compressibility varying with frequency) we should expect a corresponding dispersion of acoustic velocity in the vicinity of the ' relaxation frequency '. This has been amply verified in gases where anomalous acoustic damping accompanied by dispersion of acoustic velocity have been established beyond doubt.

When we come to the case of liquids, we should, at least to a first approximation, expect similar phenomena ; only on account of the altered conditions, the frequency region of anomalous damping will shift. The molecules can no longer be treated as chaotically distributed as in gases. The anomalous acoustic damping in liquids has been established by the ' ultra-sonic ' experiments of Biquard, Claeys, Errera, Sack, etc. Detailed papers by these investigators, together with some discussions are to be found in the *Transactions of the Faraday Society*,[6] wherein a number of possible alternative explanations have been outlined. The most fruitful of all of them, that of the possibility of the adiabatic compressibility of the medium altering with frequency has been left out of consideration for the reason that no one has so far reported any dispersion of ' ultra-sonic ' velocity in liquids. Only Bernal of Cambridge has, however, pointed out that in the absence of an adequate theory of the effect it would be unsafe to reject such a possibility out of hand.

It is natural to assume that, in a liquid the equilibrium state is maintained by exchanges of the configurations in an interval of time sufficiently long compared to the intermolecular vibrations. The order of frequency at which all these acoustic damping experiments were carried out is about a few mega-cycles per second. It is quite possible that in such short intervals of time, the configuration of the liquid has no time to keep pace with the rapid fluctuations of that order, with the result, that the 'ultra-sonic' wave undergoes considerable fluctuations during its passage within the liquid. This means that one should expect dispersion of acoustic velocity to accompany anomalous acoustic damping. The present paper dealing with the 'hyper-sonic' velocity determinations in liquids, has shown that the acoustic velocity alters considerably when we pass from the 'ultra-sonic' to the 'hyper-sonic' region.

'Ultra-sonic' velocity measurements in liquids, have been reported by a number of investigators[7] where the accuracy attainable is decidedly great, compared to that attainable at present in the 'hyper-sonic' region. But the change expected in the 'ultra-sonic' velocity even for a change of the frequency of the order of 10 mega-cycles per second is so small (a couple of metres per second) that the temperature of the liquid has to be maintained perfectly constant throughout the series of experiments at different frequencies. Accurate measurements of 'ultra-sonic' velocity in liquids at different frequencies taking elaborate precautions for maintaining a constant temperature would appear to be well worth-while.

In the 'hyper-sonic' region where we are dealing with frequencies of the order of 10^9 cycles per second, the change in velocity from the 'ultra-sonic' to the 'hyper-sonic' value is as much as in excess of 150 metres per second in liquid carbon tetrachloride and a diminution by about 225 metres per second in liquid acetone. In spite of the allowable error in measurement being taken to be as high as $0{\cdot}010\,\text{cm.}^{-1}$ (four times the usual allowable error) which corresponds to a difference in the measured velocity by ± 25 metres per second the fact that the acoustic velocity changes by as much as 200 metres per second definitely establishes the dispersion of acoustic velocity in liquids. This is why 'hyper-sonic' velocity determinations in liquids are very necessary at the present moment.

Another important point to be remembered is that it is not necessary that the 'hyper-sonic' velocity should always be greater than the 'ultra-sonic' velocity. The fact that in the case of carbon tetrachloride the 'hyper-sonic' velocity is greater than the 'ultra-sonic' velocity in contrast to that in acetone shows that the 'relaxation frequency' in liquid carbon tetra-

chloride is far greater than that in liquid acetone and that the adiabatic compressibility in acetone has at the 'hyper-sonic' region come down to its normal value corresponding to that at very low frequencies. In the case of carbon tetrachloride the 'relaxation frequency' must be very near the 'hyper-sonic' region. By way of illustrating the above point, let us examine the anomalous damping coefficients in these liquids as recorded by the several investigators. Within the frequency range 0·287 mega-cycles per second and 11·4 mega-cycles per second, the observed and calculated acoustic damping coefficients agree very well in the case of carbon tetrachloride, while in acetone the observed damping coefficient is nearly four times the one calculated from the classical hydrodynamic formula of damping. But according to the latest measurements of acoustic damping in liquids at still higher frequencies of the order of 80 mega-cycles per second,[8] it is found that while in acetone the observed damping coefficient is still of the same order as before, in liquid carbon tetrachloride, however, the observed acoustic damping coefficient has suddenly jumped up to nearly twenty times the normal value, showing thereby that the frequency of 54 mega-cycles per second is very near its 'relaxation frequency'.

This paper is intended to establish the presence of dispersion of acoustic velocity with frequency in the case of two typical liquids in the first instance, which have stood the test of careful repetition and scrutiny. Investigation on similar lines are being carried out in various other liquids and their results will shortly be reported in subsequent communications.

In conclusion, the author desires to express his grateful thanks to his Professor Sir C. V. Raman, for his kind interest in his work.

5. *Summary.*

The present paper deals with the acoustic velocity determinations of 'hyper-sonic' waves by a study of the fine structure of the radiations scattered by liquids under suitably controlled experimental conditions like the use of a specially designed, low density, cathode-cooled, mercury vapour lamp and a proper selection of the invar distance piece of the etalon employed with reference to the sound velocity in the particular liquid under examination and the radiation employed. The results indicate the presence of dispersion of acoustic velocity in liquids with frequency in the case of two typical liquids like carbon tetrachloride and acetone which have stood the test of careful repetition and scrutiny. These results are discussed at some length and their bearing on the hitherto unexplained anomalous acoustic damping in liquids in the 'ultra-sonic' region is indicated.

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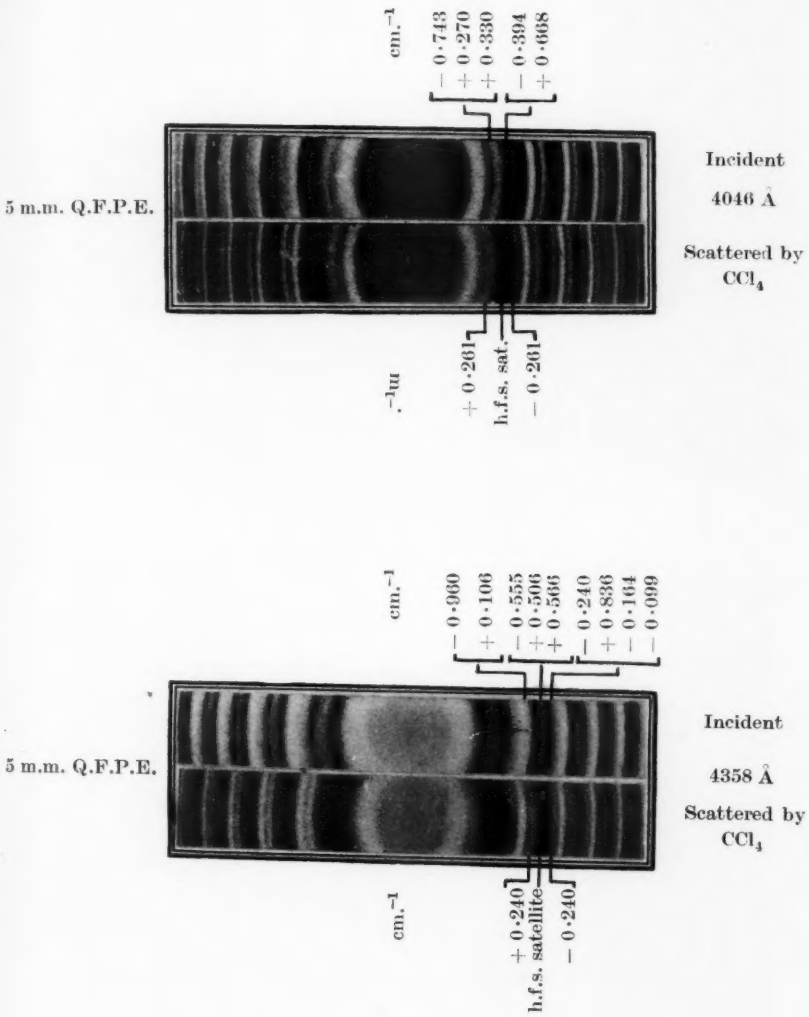
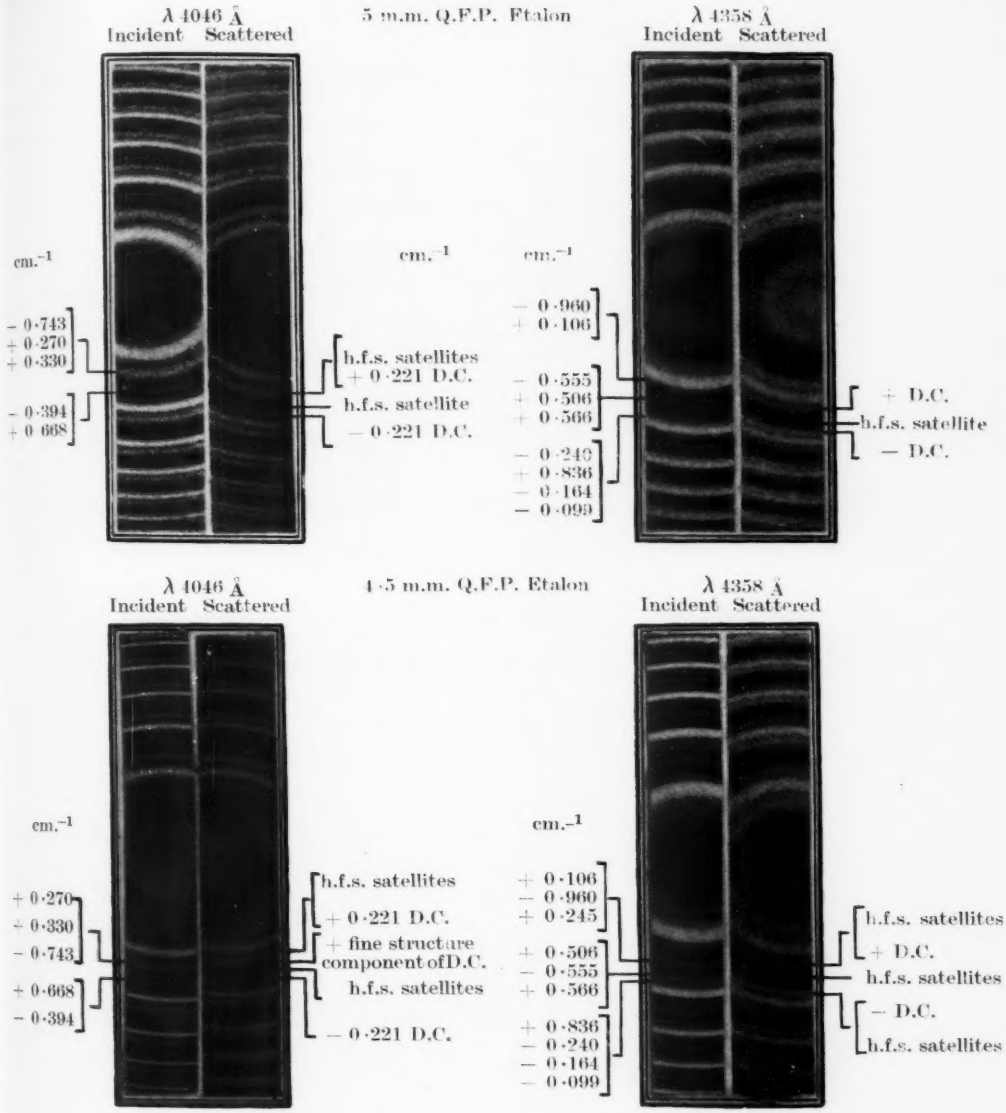


Fabry-Perot Patterns of radiations scattered by carbon tetrachloride.



Fabry-Perot Patterns of radiations scattered by acetone.

ON A TRIGONOMETRIC SUM.

By S. Chowla,
Government College, Lahore.

Received February 24, 1938.

The following lemma was incompletely proved in an unpublished MS.* of Hardy and Littlewood, concerning the magnitude of the difference between consecutive primes.

Lemma α. *If* q *is large,* $k = 0(\log q)$, *then*

$$(1) \qquad S = \sum_{\substack{0 < p < q \\ (p, q) = 1}} \frac{\sin^2\left(\frac{k\pi p}{q}\right)}{\sin^2\left(\frac{\pi p}{q}\right)} > (1 - \delta)\, k\phi(q)$$

where $\delta > 0$ *is arbitrarily small,* $q > q_0(\delta)$; $\phi(q)$ *is Euler's totient function.*

I prove here the sharper result :

Lemma β.

$$(2) \qquad S = k\phi(q) + O(k^{3+\epsilon})$$

where $\epsilon > 0$ *is arbitrary* ; (2) *shows that* (1) *is true if, for example,*

$$k < q^{\frac{49}{100}}, \qquad q > q_0(\delta).$$

Proof of (2) : We know that

$$(3) \qquad n + 2 \sum_{m=1}^{n} (n - m) \cos mx = \frac{\sin^2\left(\frac{nx}{2}\right)}{\sin^2\left(\frac{x}{2}\right)}.$$

Putting $n = k$, $x = \frac{\pi p}{q}$ here, we get

$$(4) \qquad \sum_{\substack{(p, q) = 1 \\ p < q}} \frac{\sin^2\left(\frac{k\pi p}{q}\right)}{\sin^2\left(\frac{\pi p}{q}\right)} = k\phi(q) + 2 \sum_{r=1}^{k} (k - r)\, g(r)$$

* On the basis of the unproved extended Riemann hypothesis it is proved there that $\frac{p_{n+1} - p_n}{\log n} < \frac{2}{3} + \delta$, for infinitely many n, where p_n is the nth prime. Prof. Littlewood kindly lent me the MS. in 1931.

where

$$g(r) = \sum_{\substack{(p,q)=1 \\ p<q}} \cos \frac{\pi p r}{q}.$$

From satz 220 of Landau's *Vorlesungen über Zahlentheorie*,

$$g(r) = O(r^{1+\epsilon}) \tag{5}$$

where $\epsilon > 0$ is arbitrary.

(4) and (5) prove (2).

CHEMICAL EXAMINATION OF *ERYTHRINA INDICA*.

By P. Suryaprakasa Rao, C. Venkata Rao
and
T. R. Seshadri.
(*From the Department of Chemistry and Technology, Andhra University, Waltair.*)

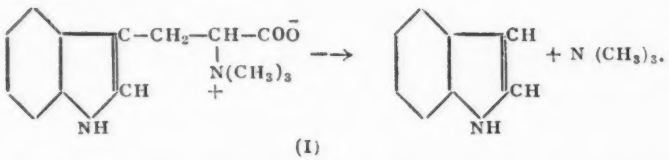
Received February 14, 1938.

Erythrina indica is known as the Indian Coral tree (English), *Parijata* (Sanskrit), *Pangra* (Hindi) and *Badita* (Telugu). The bark, the leaves and the seeds have long been used in the treatment of diseases and various valuable properties are attributed to them (Watt).[1] An attempt at a systematic investigation of the bark was made by Chopra, Ghosh and Sen in 1934.[2] From an alcoholic extract they isolated an impure alkaloid (0·05%) as a dark coloured varnish-like mass decomposing at 97° and two other water-soluble bases betaine and choline besides mineral matter chiefly potassium chloride and carbonate and a large quantity of resin. A preliminary chemical examination of the leaves was made by Chakravarti, Sitaraman and Venkatasubban[3] who noticed that besides the usual components the leaves contained a substance of a complex nature melting at 83° C. and a mixture of alkaloids, one of which was isolated and found to melt at 117° C. No work on the composition or properties of these seems to have been done. Kafuku and Hata[4] made a chemical study of the fixed oil present in the seeds collected in Formosa. No definite information is available about the chemistry of the basic components of the seeds except that they contain a poisonous alkaloid of unknown nature (Greshoff).[5]

From a study of the past literature it seemed to be possible that the seed, bark and leaf contain water-soluble alkaloids and hence attempts have now been made to isolate and identify them. A good sample of the seeds collected from the surroundings of Waltair was first extracted with light petroleum in order to isolate the fixed oil. In yield as well as in most of its properties the oil agreed closely with the sample examined by the Formosan workers. Ours however, had a lower iodine value and a higher solid acids content. The difference may be attributed to the influence of locality and climate.

The oil-free seeds yielded to alcohol a water-soluble alkaloid which formed a sparingly soluble nitrate melting at 220–22° C. It was found to reduce potassium permanganate and ferric chloride very readily, gave an intense violet colour with glyoxalic acid and sulphuric acid and underwent

decomposition with aqueous potash to yield trimethylamine and indole. It was therefore surmised to be hypaphorine, an alkaloid first isolated by Greshoff from *E. hypaphorus* whose constitution as (I) was established by Von Romburgh and Barger.[6] The identity was established by comparison with an authentic sample of the nitrate kindly supplied by Prof. G. Barger, F.R.S., in regard to crystal structure, melting and mixed melting points and optical rotation.



(I)

The bark was examined in two ways. In one experiment the powdered bark was extracted directly with ethyl alcohol and in the other it was subjected to an additional preliminary extraction with cold ether. This modification did not produce any marked difference in the nature of the two extracts. On removing the alcohol the residue gave marked reactions for alkaloids. There was, however, plenty of resinous and mineral matter. The basic portion was found to be easily soluble in water and gave all the reactions for hypaphorine. But attempts to isolate the sparingly soluble nitrate ended in failure. It was felt that this was due to the large admixture with resin and mineral matter which made the separation impossible. The water-soluble portion of the alcoholic extract was therefore decomposed with boiling aqueous potash and the volatile products of decomposition were distilled and examined. Indole was found to be one of the products. A strongly basic water-soluble portion was converted into the chloroplatinate and the product examined. It was found to be a mixture of the chloroplatinates of trimethylamine and ammonia. The formation of indole and trimethylamine showed the presence in the bark of hypaphorine. The production of ammonia is obviously due to the decomposition of some accompanying plant substances. It is known that the amino-acid tryptophane gives the same colour reactions as hypaphorine. But it does not decompose into indole with aqueous alkali under the conditions employed.

The leaves also were found to contain hypaphorine as water-soluble substance. But it was not possible to isolate it owing to the same difficulties as in the case of bark. Further the amount of it present seemed to be much smaller.

With regard to the chemistry of other species of *Erythrina* reference should be made to the work of Maranon and Santos on *Erythrina variegata*[7]

and of Folkers and Major[8] who very recently claim to have isolated a new alkaloid named erythroidine from *Erythrina americana*.

Experimental.

Seeds:

The fixed oil.—A good sample of the seeds was collected from the neighbourhood of Waltair, powdered and extracted with light petroleum (60–70°C.) in a Soxhlet extractor for 6 hours. When the operation was conducted vigorously this period was found to be sufficient for completely removing the fixed oil from the crushed seeds. The light petroleum solution was dried over fused calcium chloride, filtered and the solvent distilled off. The last traces of petroleum were removed by bubbling a current of nitrogen through the oil. Thus was obtained a pale yellow oil in a yield of about 11·3% of the air-dried seeds. On allowing it to stand for a week, a small quantity of a solid in the form of glittering flakes settled down. As much of the clear oil as possible was decanted off and the rest filtered off in order to separate this solid for examination. It was however too small to permit detailed study; it seemed to be a fairly high melting plant wax.

The physical and chemical properties of the fatty oil were determined and the values are given below along with those obtained for the oil from the Formosan seeds for purposes of comparison.

	Waltair Seeds	Formosan Seeds
Density	0·8821 at 30° C.	0·8964 at 40° C.
Refractive index ..	1·4596 at 30° C.	1·4604 at 40° C.
Acid number	1·24	2·95
Saponification value ..	184·5	184·5
Iodine number	63·3	71·94
Unsaponifiable matter ..	0·81	0·497
Melting point	20–21° C.	..

The two samples agreed closely in most of their properties except in their iodine value. This may be the result of climatic differences which are known to have considerable effect on the degree of unsaturation of the fixed oils of seeds.

About 5 to 10 grams of the oil were saponified in the usual way using alcoholic potash (25 c.c.). After the saponification the soap was dissolved in sufficient quantity of water and boiled in a conical flask to remove as much alcohol as possible. It was then decomposed with dilute sulphuric acid, the liberated acids were made to separate on the top by continued boiling and the aqueous layer syphoned off. The fatty acids were repeatedly washed with water to remove all the mineral acids (tested with methyl orange). The whole was then filtered, the acid portion on the filter dried, dissolved in petroleum and after evaporating off the solvent weighed. The insoluble fatty acids formed 95·1% of the fatty oil.

As the oil seemed to contain very little resin no attempt was made to estimate resin acids. Separation of the saturated and the unsaturated fatty acids was effected by Twitchell's lead salt method.

	Waltair Seeds	Formosan Seeds
Saturated fatty acids ..	36·7	30·7
Unsaturated fatty acids ..	63·3	69·3

The higher percentage of saturated fatty acids in the Waltair sample accounts for its lower iodine value.

Since it has been stated by the Formosan workers that the unsaturated fatty acids are mainly linolic and oleic acids, the thiocyanogen value of our sample was determined with a view to calculate the proportions of the two acids. It was found to be 54·7 and the percentages of linolic and oleic acids as obtained from a calculation using this value are : oleic acid 84·4% and linolic acid 15·6% (Kafuku and Hata, oleic acid 80% and linolic acid 20%). The thiocyanogen value further leads to the calculated figure 36·7 for the saturated fatty acids which agrees with the value obtained by direct estimation. The lower linolic acid content and the higher saturated acid percentage of our samples thus accounts for its lower iodine value.

Isolation of an alkaloid, Hypaphorine.—The powdered seeds (500 gr.) that had been extracted with light petroleum were boiled under reflux with alcohol twice, six hours each time and the extract so obtained was distilled to remove almost all the alcohol. The residue was taken up with a small volume of hot water (30 c.c.) and filtered after cooling. The aqueous extract gave good tests for the presence of an alkaloid with Meyer's reagent and with phosphomolybdic acid. On acidifying the clear aqueous extract with

concentrated nitric acid (5 c.c.) a colourless crystalline precipitate was deposited rapidly. It was filtered. The mother-liquor gave no more solid on further addition of acid. The precipitated solid was dissolved in a small volume of hot water, filtered and acidified with nitric acid. The nitrate crystallised out as colourless flat needles and prisms melting at 220°–22° C. A further crystallisation as above rendered the salt quite pure, the melting point being raised to 222°–24° C. The yield of the pure salt was 1·2% of the weight of the whole seed. (Found: C, 54·0; H, 6·4; N, 13·9%; $C_{14}H_{19}N_3O_5$ required C, 54·4; H, 6·1; N, 13·6%.)

The substance was found to possess strong reducing properties. It decolorised potassium permanganate and reduced ferric chloride to the ferrous salt. It gave an intense violet colour with glyoxalic and sulphuric acids. When heated with aqueous potash (10%) it underwent decomposition into indole and trimethylamine. After decomposition the alkaline liquid was distilled to half its volume and in the distillate indole was identified by its reactions with sodium nitroprusside and para-dimethylaminobenzaldehyde. By collecting the distillate in aqueous hydrochloric acid, ether-extracting the solution to remove neutral products, concentrating it to a small bulk and treating with platinic chloride the chloroplatinate of trimethylamine was obtained. It melted at 236–38° C. and was found to be identical with a sample prepared from trimethylamine, the mixture melting also at the same temperature.

The alkaloid therefore seemed to be hypaphorine and its identity was established by comparison of the nitrate with an authentic sample of alkaloid nitrate kindly provided by Prof. G. Barger, F.R.S. The two samples were found to be identical in crystal structure (colourless flat needles and plates), to have the same melting point 222°–24° C. (Romburgh and Barger 215–20°) which was unaffected by admixture, and the same optical activity $[\alpha]_D$ 95·0° (Romburgh and Barger, 94·7°).

The residual cake.—The residue of the powdered seeds left after the removal of oil and hypaphorine was ashed in a platinum basin. It gave 4·2% of ash which was found to consist mainly of calcium, magnesium and potassium salts of phosphoric acid along with small quantities of chloride and some silica. The total nitrogen in the cake was 6·5% indicating that the proteins form about 40%.

Examination of the bark.—The bark offered difficulties in powdering since the inner portions consisted of tough fibre. It was therefore cut into small bits when fresh and then powdered after drying. About 7 kilograms of the bark were extracted with alcohol, each lot being boiled twice for

6 hours each time. When the extract was concentrated a large quantity of a colourless crystalline solid separated out. This consisted of mineral matter being mostly potassium chloride and carbonate. It was filtered off and alcohol evaporated as completely as possible. A voluminous dark brown semi-solid was left behind. This was extracted with about 50 c.c. of hot water and filtered. The brown aqueous extract gave good tests for alkaloids. A second extraction using about 20 c.c. of water removed a further small quantity of the basic substance, the residual resin retaining only insignificant amounts. This solution gave all the tests for the presence of hypaphorine.

Addition of concentrated nitric acid to the aqueous extract precipitated only resinous matter and no crystalline solid was produced. On the other hand, some decomposition with evolution of gas was noticed. With a view to isolate the base as the hydrochloride another portion of the aqueous extract was acidified with hydrochloric acid, the precipitated resin filtered off and the solution concentrated in a vacuum desiccator. The residue was found to be contaminated with a large amount of mineral matter and could not be purified.

The water-soluble basic portion was therefore treated with 10% aqueous potash and distilled till about half the volume of the liquid came over. The distillate which was strongly alkaline gave the requisite tests for indole whereas the original aqueous extract did not give the tests. When the distillate was rendered acid with hydrochloric acid, extracted with ether repeatedly to remove non-basic matter, concentrated to a small bulk and treated with a solution of platinic chloride, a yellow crystalline chloroplatinate was obtained. It melted almost completely between 230–35° though a small amount was left behind and it decomposed much higher. When boiled with a large volume of alcohol the insoluble residue melted at 236–38° and was found to be identical with the chloroplatinate of trimethylamine whereas the small portion that went into solution in alcohol was identified as the chloroplatinate of ammonia. The basic volatile matter therefore consisted mostly of trimethylamine along with a small amount of ammonia. It was therefore concluded that hypaphorine was present in the bark. This was supported by the colour reactions given by the aqueous extract mentioned above. The only other substance that can give these reactions is tryptophane. But this substance does not undergo decomposition under the conditions described above. The small amount of ammonia detected probably arose from an accompanying impurity. The bark gave about 15·5% of ash and the alcohol extracted a good portion of the mineral matter.

The leaves.—About 4 kilograms of the dry leaves were powdered, extracted with alcohol and the water-soluble portion of this extract examined as in the case of the bark. No sparingly soluble nitrate could be isolated though the extract gave prominent reactions for hypaphorine. It contained much more of impurities giving rise to ammonia on decomposition with alkali so that it was difficult to isolate trimethylamine chloroplatinate. Indole was, however, produced as one of the decomposition products thereby confirming the presence of hypaphorine.

Summary.

From the seeds of *Erythrina indica* a fixed oil and a water-soluble alkaloid have been isolated. The properties of the oil have been compared with those of the oil of the Formosan variety and found to differ in the degree of unsaturation. The alkaloid has been identified as hypaphorine. The bark contains, besides a large amount of mineral matter and resin, the same base which is also present in the leaves to a smaller extent.

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STUDIES ON THE SPREADING OF CERTAIN SUBSTANCES ON A CLEAN SURFACE OF WATER—PART I.

By L. A. Ramdas (*Poona*)
AND
P. S. Vaidyanathan (*Nagpur*).

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1. Introduction.

In a paper entitled " On the origin of the movements of camphor on water and other allied phenomena,"[1] published in 1926, one of us put forward an explanation for the movements of solid substances like camphor and antipyrin and of liquids like amyl alcohol when placed on a clean surface of water. Soluble organic compounds, whether solid or liquid, which are active on a clean water surface spread as mono-molecular films on the water surface and disappear quickly by solution into the water below or by evaporation into the space above. When a piece of the solid or a drop of the liquid floats on water the spreading is continuously maintained. The phenomena taking place may be observed directly by dusting the surface of water with lycopodium. The dust particles are swept out by the advancing film and a clear area is maintained around the source. The continuous streaming of the film in the clear area and the compensating movements set up in the dusty area outside it together provide a vivid picture of the phenomenon of spreading. The mono-molecular streaming begins at the edge of the substance where it is in contact with the water surface* and the movement is at right angles to the edge. The stream lines are found to be convergent when the edge is concave and divergent when it is convex. In the former case the packing of the molecules in the surface film is denser and the surface pressure greater than in the latter case, as verified by actual measurement. Consequently the floating particle or lens moves away from the concave side. In fact, movement of the floating body takes place only when the field of spreading round it is non-uniform.

Since 1926 a considerable amount of literature on the subject of surface films has grown up.[2,3] The interesting work of Cary and Rideal on the

* We shall hereafter refer to the boundary of a floating substance where it is in contact with the water surface as the " perimeter of contact".

spreading of insoluble long-chain compounds may also be referred to. It may be pointed out, however, that after the classical work of Miss Pockels[4] so long ago as 1891, not much quantitative work appears to have been done on certain aspects of the subject. Miss Pockels was the first to observe, for instance, that a clean surface of water really possesses a higher dissolving power as is shown by the experiment in which a thin disc of camphor so hung that it is half immersed in water is cut through in the course of a few hours. The present investigation was taken up with a view to examine quantitatively how "Surface solution" differs from "Internal solution" in the case of a soluble substance like camphor, and how the former effect depends upon (1) the area of the camphor block, (2) its perimeter of contact, (3) the area of the water surface and (4) the depth of the column of water. The mechanical effects of a spreading film on the stability of the water layers below have also been observed by means of an optical method. The results obtained so far are described in the following pages.

2. *Surface Solution and Internal Solution.*

In these and some of the subsequent experiments circular glass vessels, 13 cm. in diameter and 8 cm. in height, with 6 cm. depth of water are used. Clean surfaces of water are obtained by overflowing tap water in the vessels (previously cleaned with soap) and blowing off the top layer suddenly. The camphor blocks used were initially 1·25 cm. square and about 2 mm. thick. To eliminate the effect of evaporation or sublimation of camphor, the vessels are kept covered with close fitting lids during the experiments.

A piece of camphor is allowed to float on a clean surface of water in a vessel A and another kept immersed in water in vessel B. The camphor in A continuously moves about so that the surface solution takes place more or less uniformly from all points on the edges, although at a given moment, it takes place only from the perimeter of contact at that instant. It took 16 hours 23 minutes for 0·3296 gr. of camphor in A to disappear by surface solution whereas in the same interval the camphor in B, weighing initially 0·3361 gr. lost only 0·0561 gr.

Having ascertained the order of magnitude involved, the next experiment was arranged so as to obtain the rate of solution of similar camphor pieces kept as indicated below:—

(*a*) One piece of camphor weighing 0·1737 gr. was kept on a clean surface of water in vessel A, the water below being renewed once every hour in order to minimise the effect of change of concentration of camphor in water below on the rate of surface solution.

(*b*) A second piece of camphor weighing 0·1671 gr. was kept *immersed* in water in vessel B.

(*c*) A third piece of camphor weighing 0·1531 gr. was kept *floating* on a water surface contaminated with oil in vessel C ; the edges of the camphor block in this case are inoperative as no surface solution can occur on the greasy surface of water. The camphor will, however, undergo internal solution from its surface below which is in contact with water.

The camphor in vessel A was removed at the end of each hour and weighed after drying in a desiccator, care being taken to prevent sublimation from it by keeping a few other pieces of camphor permanently in the desiccator so as to ensure a saturated atmosphere of camphor inside. From curve (*a*) in Fig. 1 it will be seen that it took 6 hours and 40 minutes for the camphor on the clean surface of water to disappear completely. Further

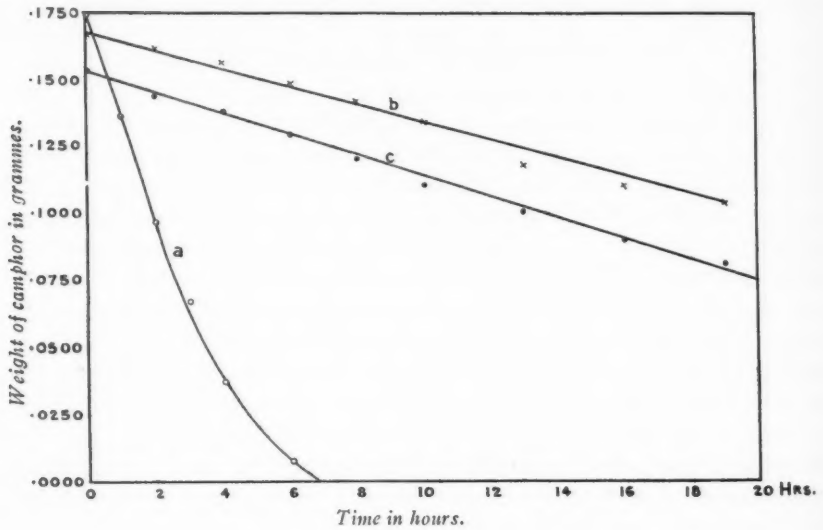

Fig. 1.

Variation in weight of camphor pieces (*a*) floating on a clean surface, (*b*) immersed in water and (*c*) floating on an oily surface of water.

the loss of weight per hour is much more at the beginning of the experiment than at the later stages. Curves (*b*) and (*c*) in Fig. 1 represent the rates of change in weight of the camphor pieces in vessels B and C. The rates of solution in both these cases are much smaller than in the previous case.

They are, however, uniform and more or less similar to each other. The experiment in vessel C provides an estimate of the rate of internal solution vertically downwards from the bottom of the floating piece of camphor into the water below. From the present experiment as well as a similar experiment with a bigger piece of camphor, it is observed that the rate of this solution is 0·0062 gr. per sq. cm. per hour. The values of the loss of weight indicated by curve (*a*) in Fig. 1 have to be corrected at the above rate so as to obtain an estimate of the rate of surface solution alone in vessel A. This correction which is proportional to the area of contact of the camphor with water has been applied to all estimates of surface solution discussed hereafter. It may be remarked that in experiment (*a*) [*vide* curve (*a*), Fig. 1] the size of the camphor piece is continuously varying with time. The influence of such variation on the rate of solution requires investigation.

3. *Relation between the Rate of Surface Solution and the Perimeter of Contact.*

Preliminary experiments showed that the area swept out by the films spreading from the edges of a camphor block on water increases with the size of the camphor. In order to find out how exactly the rate of surface solution depends upon the size, camphor pieces of different sizes were allowed to float on similar surfaces of clean water and their changes in weight, area in contact with water, and the perimeter of contact with the water surface determined at the end of each hour. The experiments were repeated for a wide range of values of the variables. The complete results are set out in Table I: In Table I, the first column gives the mean perimeter of the camphor block during an hour in cm., the second column gives the mean area during an hour in square centimetres. The third column gives the total loss of weight per hour in grammes. In the next column the small corrections for direct solution (proportional to the area) are given. The last column gives the actual weight of camphor lost by surface solution in grammes per hour. It may be noted that the values of the perimeter decrease progressively from the top of column 1 to the bottom. Some of the values of the area do not vary in the same direction because the perimeter of the camphor was in some cases varied without changing the area, by merely altering the shape suitably. It is found that the rate of surface solution does not depend upon the area or the shape of the camphor, but only on the perimeter. The values of perimeter are plotted against the rate of surface solution per hour in Fig. 2. It is interesting to note that the relationship is linear and that the rate of surface solution is ·0096 gr./hr./cm. or $2·67 \times 10^{-6}$ gr./sec./cm.

TABLE I.

Table showing the weight of camphor dissolved per hour by surface solution on water.

Mean perimeter of camphor in cm.	Mean area of camphor face in contact with water in sq. cm.	Total loss of weight per hr. in gr.	Estimated loss of wt. of camphor by direct solution in gr.	Wt. of camphor dissolved per hour by surface solution alone in gr.
9·68	2·93	·1090	·0182	·0908
8·89	2·47	·1006	·0154	·0846
8·29	2·15	·0914	·0134	·0780
6·83	1·08	·0722	·0066	·0656
5·95	0·778	·0626	·0055	·0571
4·76	1·42	·0541	·0088	·0453
4·84	1·46	·0540	·0091	·0449
4·48	1·26	·0500	·0078	·0422
4·29	1·15	·0484	·0071	·0413
4·17	1·09	·0480	·0067	·0413
3·93	0·965	·0394	·0060	·0334
3·57	0·709	·0390	·0044	·0346
3·17	0·533	·0374	·0034	·0340
3·13	0·614	·0326	·0038	·0288
2·62	0·378	·0286	·0027	·0259
2·14	0·287	·0236	·0019	·0217
1·63	0·165	·0158	·0009	·0149
1·19	0·088	·0136	·0007	·0129

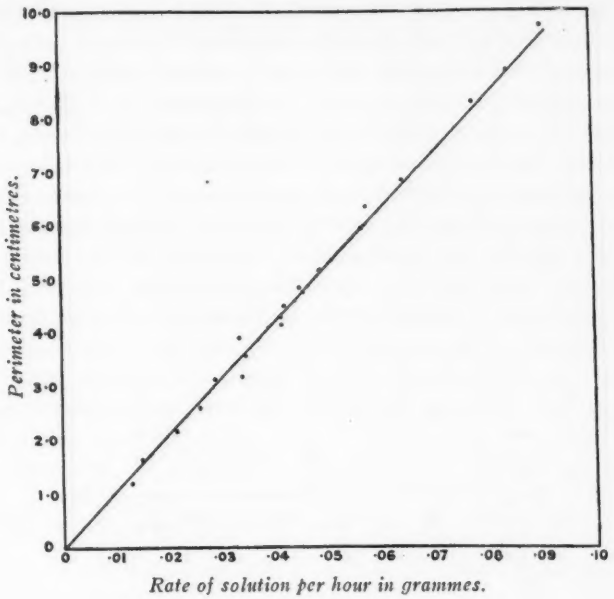

FIG. 2.

Linear relation between the perimeter of contact and rate of surface solution.

4. Relation between the Rate of Surface Solution and the Area of the Water Surface.

We may now consider the effect of the area of the water surface on the rate of surface solution. In this series of experiments camphor blocks having the same shape and perimeter equal to 5 cm. were placed on clean surfaces of water having areas of 45, 135 and 718 sq. cm. respectively. The loss of weight due to surface solution was ascertained at the end of one hour. These were all found to be of the order of 0·05 gr. per hour showing that the area of the surface of water on which spreading can take place has no sensible effect on the rate of surface solution. This suggests that whatever be the area of the water surface, once a layer of camphor molecules leaves the edge of the block, it should spread on the water and go into solution in such a manner as not to affect the subsequent layers, in their rate of leaving the edge and spreading on water.

In order to see what happens during spreading in the case of extensive and of restricted surfaces, clean surfaces of water in glass vessels of different cross-sections are used. The movements on the surface of water as well

as in the water below when spreading occurs can be observed if a beam of sunlight is focussed on the water surface from below at an angle greater than the critical angle so that the beam is totally reflected. The beam is focussed on the water surface so that the incident and reflected beams are symmetrical. On dusting the water surface with lycopodium it is noted that when the area of the surface is very large, the mono-molecular film goes on spreading on the surface up to a certain diameter, the molecules of the film disappearing into the water below more or less quickly at the periphery of the area of spreading. When the area of the water surface is reduced to 50 sq. cm. or so, the spreading of the film proceeds right up to the sides of the vessel; the film which is obstructed by the sides now turns down quickly into the water below setting up a vigorous convection pattern therein. A vertical section of the convection and the spreading on the surface is shown in Fig. 3. The spreading occurs along OA and

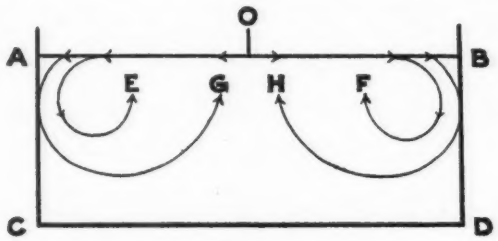

FIG. 3.

Type of convection induced in the body of a liquid column by mono-molecular spreading at the surface.

OB but the films turn into the water as OE and OG and OF and OH respectively. The lycopodium particles which are also swept down into the water along with these currents show the nature of the movements very vividly. The motion is a slow rising one from below towards the neighbourhood of the camphor block.

The abruptness with which a spreading film of camphor moves downwards at the outer limits of a restricted area is indeed remarkable. The appearance is very striking if a drop of a coloured solution of non-spreading material is placed gently on the surface of water, when it is carried away along the surface and pushed down at the boundary of the spread area and mixed up with the water below by the convection currents which are set up. We thus see how the spreading film is disposed of whatever be the area offered for spreading and how the perimeter of contact appears to be the only factor which matters.

There is another aspect of the matter which deserves consideration. In work on spreading mono-molecular films the phenomena taking place in the water below appear to have been overlooked. From the usual experiment one gets the impression that a mono-molecular film spreading on a clean water surface does not cause any movements in the water below. Careful observations of the movements of the motes in the water just below the surface with the optical illumination referred to earlier, show that the spreading at the surface does cause a viscous drag in the adjacent water layers below, whatever be the extent of the surface. It is therefore clear that a part of the energy of spreading is used up against the viscous forces which are associated with the laminar flow parallel to the surface in the water layers adjacent to the surface and in the vortex-like convection below the periphery of the spread film. The effect of these movements can be seen even several centimetres below the water surface. We thus see that the phenomenon of spreading is associated with a considerable amount of agitation and consequent mixing in the water column below the surface.

5. Variation of Surface Solution with Depth of the Water Layer.

The fact that the rate of loss of camphor depends mainly on the perimeter of contact is further confirmed by experiments on the influence of the depth of the water on the rate of surface solution. The results of the experiments are given below :—

TABLE II.

Depth of water in cm.	Weight of camphor lost by surface solution in half an hour by camphor pieces with a perimeter of 5 cm.
·32	0·0268 gr.
·63	0·0297 gr.
1·25	0·0291 gr.
2·50	0·0296 gr.

We therefore see that the depth of the water has little influence on the rate of surface solution.

6. *Influence of a Spreading Mono-molecular Film on Evaporation from a Water Surface.*

It is well known that an evaporating surface of water is slightly cooler than the water below. Our measurements using a pair of very fine thermal couple junctions of copper and constantan (both of gauge 50 s.w.g.) and a Moll's micro-galvanometer (which records the deflections within 0·2 second) show that this cooling varies from a fraction of a degree to several degrees Centigrade, depending upon the rate of evaporation. On allowing a mono-molecular film of camphor or of any other soluble substance to spread on the surface of water it is found that the deflection in the galvanometer due to the initial temperature difference decreases almost instantaneously to a value near zero and remains so as long as the film is spreading. On removing the source of the spreading film the deflection again assumes its original value. The effect is only temporary in the case of a film of insoluble substance like palmitic acid or oleic acid, where, after the spreading is over, a permanent film is left behind. At first sight it appeared that the effect associated with a spreading film, may be due to either (*a*) the evolution of heat as " heat of spreading " or (*b*) a suppression of evaporation by a spreading mono-molecular film. The first explanation was negatived by repeating the experiment inside a glass chamber containing air saturated with water vapour when, owing to the absence of evaporation, the galvanometer showed no deflection ; on spreading a film of camphor, it was found that the galvanometer deflection was still zero, showing that no heat is evolved at the surface. To verify whether a spreading film causes a decrease of evaporation from a water surface, two glass vessels of identical dimensions and the same quantity of water with clean surfaces were taken. After weighing initially, both were kept uncovered to permit evaporation to take place. In one of the vessels a small quantity of anti-pyrin which spreads on a water surface, was dropped at intervals so as to maintain a spreading film. After an interval the vessels were weighed again. In one case the difference in weight indicated the evaporation from the surface of pure water and in the other case, after allowing for the weight of anti-pyrin dropped, the evaporation from a water surface in which a film of antipyrin was continuously spreading was obtained. The experiment was repeated several times and invariably it was found that *more* evaporation took place from the surface of water with a spreading film than from the pure water surface. For example, in one experiment the evaporation from the pure water surface was 0·0114 gr. whereas in the case of the water surface covered by a spreading film the evaporation was 0·0138 gr. during an interval of 25 minutes. When the experiment in

which the movements of water layers below a spreading film are examined optically was repeated it became clear that the whole phenomenon admits of a simple explanation on the basis of the convection in the water below the surface. The mixing associated with these internal movements is sufficiently rapid and efficient to equalise the temperatures of the evaporating water surface and of the water below respectively. As a result the temperature of the evaporating surface would be higher than in the case of the pure water surface and it is easy to see why the evaporation should be also slightly greater.

The investigations on these surface phenomena are being continued. The rôle of the convection associated with surface spreading on the damping effect on waves on a water surface is also under investigation.

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EFFECT OF TEMPERATURE ON THE RAMAN SPECTRUM OF LIQUID CCl_4.

Some Preliminary Considerations.

By R. Ananthakrishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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1. Introduction.

In a note published in *Current Science*, for June 1936, the author reported some preliminary observations relating to the spectral changes noticed when the Raman spectrum of liquid CCl_4 was photographed at a series of temperatures extending over an interval of about 200° C. Although during the subsequent months time and attention were devoted towards a closer study of this problem, it has not been possible to pursue it in all its details, because of other lines of work which were on hand during this period, and the author's subsequent departure from the Institute. Nevertheless, it is considered worthwhile to place on record the trend of ideas that have been pursued, and such experimental results as have been obtained during the course of the work.

The study of the effect of temperature on the Raman spectra of substances in general is a problem of interest because of its direct bearing on the important question concerning the nature of the changes brought about by heat in the condition of the molecules in such substances. Quantitative investigations in this direction have been comparatively rare, although we have a large mass of qualitative information. For instance, it is well known that the Raman spectra of polar substances often exhibit appreciable changes when the substances are examined over fairly wide intervals of temperature. These changes fall under two distinct categories, namely, (1) those due to change of state, and (2) those due to changes of temprerature without change of state. For our present purpose, we shall confine our attention mainly to the latter class of phenomena. In polar substances these changes are attributed primarily to the mutual influence of the neighbouring molecules which presumably has a functional dependence on temperature. Such a disturbing factor is only of secondary importance in the case of non-polar substances, so that the explanation for the

observed spectral changes, if any, in the Raman spectra of such substances has to be sought for elsewhere.

By far the most important of the molecular properties the consideration of which is of importance from the standpoint of Raman spectra are the rotation and vibration of the molecules. The molecular rotation besides manifesting itself as a wing to the Rayleigh or unmodified line, also imparts a definite width to some of the vibrational Raman lines. The extent of such broadening increases with rise of temperature. Again, in so far as the anti-stokes Raman lines arise from transitions in which the excited vibrational levels of the molecules are involved as initial states, their intensity might be expected to show a pronounced increase at higher temperature. In order, however, to understand the quantitative aspect of the problem it is necessary to recall very briefly Placzek's polarisability theory of the Raman effect of polyatomic molecules (1931).

2. *Theoretical.*

It is well known that the Raman effect arises from the interaction between the nuclear and electronic motions of the molecules. In order to investigate this interaction, we consider the polarisability α of the molecule which is a magnitude characteristic of the scattering electrons and their binding with the nuclei. The effect of nuclear vibration is then to alter the polarisability of the molecule.

If ν_k and ν_e are the frequencies of the nuclear and the electronic vibrations respectively and ν the frequency of the incident light, Placzek's theory starts with the assumption that $\nu_k \ll \nu_e$, $\nu_k \ll \nu$, and $\nu_k \ll (\nu_e - \nu)$. Under these circumstances, the polarisability α is a function of the normal co-ordinates q_j of the nuclei, so that we have,

$$\alpha_{(q_1 \cdots q)} = \alpha_0 + \sum_j \left(\frac{\partial \alpha}{\partial q_j}\right)_0 q_j + \tfrac{1}{2} \sum_{jk} \left(\frac{\partial^2 \alpha}{\partial q_j \, \partial q_k}\right)_0 q_j q_k + \cdots \qquad (1)$$

where the suffix 0 refers to the equilibrium configuration. When the nuclei begin to vibrate, the quantities q_j become periodic and introduce consequently a time-dependence upon α. We have then to substitute for these quantities the well-known expressions for the harmonic oscillator. If the molecule is placed in the electric fileld E of an incident light-wave of frequency ν, the induced electric moment responsible for the scattering is αE. From the expression for αE, it can be easily seen that the term in α_0 is responsible for the Rayleigh scattering, while the term in $\left(\frac{\partial \alpha}{\partial q}\right)_0$ give rise to the Raman effect. If we take the electric field of the incident light-wave to be parallel

to the x-direction, and confine our attention only to the induced moment responsible for the Raman effect, it can be shown that,

$$\left.\begin{aligned} \overline{|M_{xx}|^2}\ (v_j \rightarrow v_j + 1) &= E^2 \overline{\left(\frac{\partial \alpha}{\partial q_j}\right)_{0_{xx}}^2}\ c_j\,(v_j + 1) \\ \overline{|M_{yx}|^2}\ (v_j \rightarrow v_j + 1) &= E^2 \overline{\left(\frac{\partial \alpha}{\partial q_j}\right)_{0_{yx}}^2}\ c_j\,(v_j + 1) \end{aligned}\right\} \tag{2}$$

and

$$\left.\begin{aligned} \overline{|M_{xx}|^2}\ (v_j \rightarrow v_j - 1) &= E^2 \overline{\left(\frac{\partial \alpha}{\partial q_j}\right)_{0_{xx}}^2}\ c_j\, v_j \\ \overline{|M_{yx}|^2}\ (v_j \rightarrow v_j - 1) &= E^2 \overline{\left(\frac{\partial \alpha}{\partial q_j}\right)_{0_{yx}}^2}\ c_j\, v_j \end{aligned}\right\} \tag{3}$$

where $c_j = \dfrac{h}{8\pi^2 \mu_j \nu_j}$, μ_j = reduced mass, ν_j = vibrational frequency, v_j = vibrational quantum number corresponding to the normal co-ordinate q_j. $\overline{|M_{xx}|^2}$ and $\overline{|M_{yx}|^2}$ represent respectively the mean square of the x and y components of the electric moment which give rise to the Raman radiation of frequency shift $\pm \nu_j$, during the quantum transition $v_j \rightarrow v_j \pm 1$.

From (2) and (3) we obtain the total intensity corresponding to the transition $v_j \rightarrow v_j \pm 1$, by multiplying by the number of molecules in the initial state v_j, and transforming the moments to the corresponding intensities. If we neglect the effect of anharmonicity, then irrespective of the initial quantum number v_j all transitions $\Delta v_j = \pm 1$ give rise to radiations of the same frequency $\nu \pm \nu_j$. We therefore obtain the aggregate intensity of the stokes and the anti-stokes components by summing up over all the initial states v_j from 0 to ∞. The result is

$$I(\nu - \nu_j) = \frac{64\pi^4}{3c^3}\,(\nu - \nu_j)^4 \left\{4\,A_{1j}^2 - 7\,B_{1j}^2\right\} \frac{1}{1 - e^{-\frac{h\nu_j}{kT}}} \tag{4}$$

$$I(\nu + \nu_j) = \frac{64\pi^4}{3c^3}\,(\nu + \nu_j)^4 \left\{4\,A_{1j}^2 - 7\,B_{1j}^2\right\} \frac{1}{e^{\frac{h\nu_j}{kT}} - 1}, \tag{5}$$

where A_{1j} and B_{1j} are the invariants of the symmetric tensor $\left(\dfrac{\partial \alpha}{\partial q_j}\right)_0$.

From (4) and (5) it follows that not only the anti-stokes Raman line $(\nu + \nu_j)$ but also the stokes component $(\nu - \nu_j)$ increases in intensity as the temperature is elevated. This is because of the factors $(v_j + 1)$ and v_j in equations (2) and (3) which show that transitions between the higher vibrational states give rise to larger intensity of scattering. Fig. 1 gives a graphical representation of the variation of the intensity of the

stokes and the anti-stokes Raman lines corresponding to the frequency shift ν_j as a function of $\frac{\nu_j}{T}$.

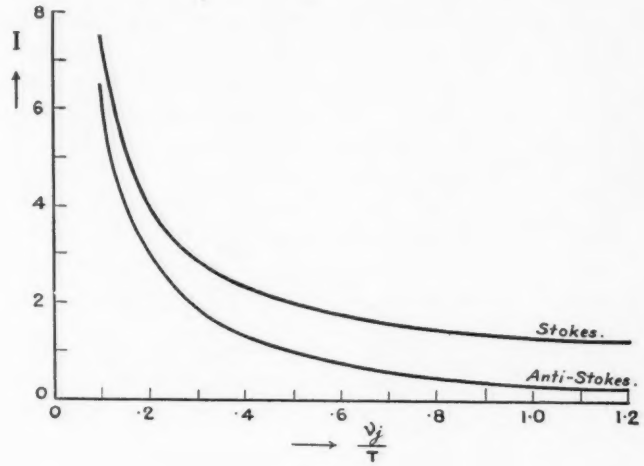

FIG. 1.

The ratio of the intensity of the stokes to that of the anti-stokes component is given by :

$$\frac{I(\nu - \nu_j)}{I(\nu + \nu_j)} = \left(\frac{\nu - \nu_j}{\nu + \nu_j}\right)^4 e^{\frac{h\nu_j}{kT}}. \qquad (6)$$

From (6) we see that the intensity of the stokes and the anti-stokes components tend to approach each other for high temperatures in conformity with the classical theory.

In the case of diatomic molecules, on account of the symmetry about the nuclear axis, the constants A_{1j} and B_{1j} in formulæ (4) and (5) can be further simplified. If we denote the polarisability of the molecule parallel and perpendicular to the nuclear axes by α and β respectively, and the inter-nuclear distance by R, and also put $\alpha - \beta = \gamma$ and $\frac{\alpha + 2\beta}{3} = \mu$, then it follows that

$$4\,A_{1j}^2 - 7\,B_{1j}^2 = 15\left(\mu'^2 + \frac{7}{45}\,\gamma'^2\right), \qquad (7)$$

where $$\mu' = R\left(\frac{\partial\mu}{\partial R}\right)_0 \text{ and } \gamma' = R\left(\frac{\partial\gamma}{\partial R}\right)_0.$$

A further approximate simplification is effected if we denote the polarisability of the individual ions (considered as isotropic) by α_1 and α_2 respectively ;

then it can be easily shown that

$$\alpha = \frac{a_1 + a_2 + \frac{4a_1a_2}{R^3}}{1 - 4\frac{a_1a_2}{R^6}}$$

$$\beta = \frac{a_1 + a_2 - \frac{2a_1a_2}{R^3}}{1 - \frac{a_1a_2}{R^6}}$$

and hence

$$\left.\begin{aligned} \mu' &= -(a_1 + a_2)\frac{12a_1a_2}{R^6} \\ \gamma' &= -\frac{18a_1a_2}{R^3}\left(1 + \frac{a_1 + a_2}{R^3}\right) \end{aligned}\right\}. \qquad (8)$$

From (4), (5), (7) and (8) we see that it is possible as a first approximation to express the intensity of the Raman lines of a diatomic molecule in terms of the polarisability of the individual atoms and the equilibrium internuclear distance.

In general, the magnitude $\left(\frac{\partial \alpha}{\partial q_j}\right)_0$ is a measure of the intensity of the corresponing Raman radiation of frequency $\nu \pm \nu_j$. If for any particular normal mode $\alpha\ (q_j) = \alpha\ (-q_j)$, then $\left(\frac{\partial \alpha}{\partial q_j}\right) = 0$, and so the intensity of the corresponding Raman radiation vanishes.

3. Survey of Previous Experimental Work.

From the above consideration, it will be seen that an experimental investigation comprising the measurement of the absolute and relative intensities of the stokes and the anti-stokes lines as a function of temperature is of great interest because it would afford a direct experimental test of the relations (4), (5) and (6) and hence also of the polarisability theory. The major part of the work in this direction has been directed towards the verification of formula (6) which gives the theoretical intensity relationship between the stokes and the anti-stokes Raman lines. The agreement between theory and experiment has been found to be generally satisfactory in this respect. It must nevertheless be clearly stressed that such an agreement by no means constitutes a crucial experimental test of Placzek's theory, because of the preponderance of the Boltzmann factor in the expression on the right-hand side of equation (6). The more difficult measurement of the variation of the absolute intensity of the stokes and the anti-stokes Raman lines might be expected to furnish some information on this point.

As early as 1928, Krishnan pointed out in a note in *Nature* that in the Raman spectram of liquid CCl_4 photographed at 81° C. the stokes lines are weaker and the anti-stokes lines brighter than in the spectrum photographed at the room temperature (34° C.). Such a result appeared to be in conformity with the semi-classical explanation of the Raman effect which existed at that time. Similar conclusions were arrived at by Brickwedde and Peters (1929) who investigated the Raman spectrum of crystalline quartz between 180° C. and 550° C. We know now that the above result, if genuine, is at variance with the demands of the quantum theory, which predicts an increase of intensity with increasing temperature for the stokes as well as for the anti-stokes Raman lines, the ratio between the two intensities at any temperature being given by the relation expressed by (6).

In 1930 Landsberg and Mandelstamm took up an experimental re-investigation of the problem in the case of crystalline quartz, and reported an increase of intensity for the stokes component of the Raman line at 465 cm.$^{-1}$ in the ratio 1 : 1·29 when the temperature was raised from 295° abs. to 810° abs. Although the expected increase was in the ratio 1 : 1·6, they concluded that the deviation was within the limits of accuracy attainable in the measurements.

More recently, Ornstein and Went (1935) published the results of an investigation of the influence of temperature on the Raman lines of crystalline quartz and calcite over a range of temperature extending from that of liquid air upto about 150° C. They noticed that while the ratios of the intensities of the stokes and the anti-stokes Raman lines were in fair agreement with equation (6), a wide discrepancy existed between theory and experiment in respect of equation (4). The absolute intensity of all the stokes lines studied by them showed a marked diminution, with rising temperature instead of the expected increase. In particular, the ratio of the intensity of the Raman line 465 cm.$^{-1}$ of quartz at 90° abs. to the intensity of the same line at 420° abs., was found to be as 1 : 0·57, while according to Placzek's theory, this ratio ought to be as 1 : 1·25. The observed diminution of intensity was much greater for the lower frequencies than for the higher frequencies. The Raman lines also showed small frequency diminutions and structural changes with increasing temperature, these being much more pronounced in the region of low frequencies. The above authors did not attempt to give an explanation of the deviations in intensity, but only remarked that due to the correspondingly small magnitude of the elastic forces between the nuclei, the low frequencies might naturally be expected to be deranged by temperature much more easily than the higher ones, and

that it is probable that Placzek's theoretical considerations are inapplicable to the lines in question.

An essential assumption underlying Placzek's theory is a chaotic distribution of the scattering centres, which, of course, can be considered to be approximated only by a liquid or a gas. It therefore appeared to be of interest to take up an investigation of the above nature with a liquid over an interval of temperature not hitherto attempted.

4. Experimental Technique and Results.

The liquid chosen was carbon tetrachloride which is specially suited for an investigation of the present type on account of the comparative simplicity of its spectrum and the remarkable chemical stability of the molecule. A convenient quantity of the liquid was distilled in vacuum into a thick-walled pyrex tube about 8 inches long and 2 cm. internal bore, capable of withstanding pressures as high as 25 atmospheres. The tube was initially degassed by heating to a high temperature with continuous evacuation by a Cenco Hyvac pump. Leaving sufficient space for expansion of the liquid at high temperatures, the tube was sealed off. The conical and rounded ends were darkened by deposition of soot, leaving a small circular aperture at the latter end for the exit of the scattered light. The tube containing the liquid was placed inside a cylindrical electrical heater which consisted of a tube of pyrex glass with sparsely wound nicrome wire, and was supported in a horizontal position at a suitable distance in front of the slit of a Hilger two-prism spectrograph. By passing suitable currents through the wire, the liquid could be maintained at any desired temperature up to 250° C. within $\pm 5°$. The illumination was supplied by a quartz mercury arc which was focussed on the liquid by means of a 6-inch glass condensing lens.

(*a*) *Frequency and Structural Changes.*—In order to follow the structural changes of the Raman lines on heating the liquid, it is necessary to work with a very narrow slit. A slit width of 0·04 mm. was employed in the present work. Photographs of the Raman spectra with sufficient intensity could be secured in 24 hours. The observed results may be summarised as follows :—

It is well known that the Raman spectrum of liquid CCl_4 consists of the following principal frequencies :—

218 cm.$^{-1}$	..	ν_2 (doubly degenerate).
314 cm.$^{-1}$	..	ν_3 (triply degenerate).
459 cm.$^{-1}$	..	ν_1 (totally symmetric).
762, 790 cm.$^{-1}$	..	ν_4 (triply degenerate).

The most striking and easily observed change brought about in the spectrum on heating the liquid is the rapidly increasing broadening and diffuseness of the Raman lines ν_4. As was first pointed out by Fermi, the splitting of ν_4 is caused by the accidental degeneracy $\nu_4 \approx (\nu_1 + \nu_3)$. At the room temperature ν_4 is a well-resolved doublet, but at 200° C. it is a broad and diffuse band extending over some 50 wave-numbers, the two components having considerably spread out and practically run into each other. The other two degenerate frequencies which are fairly sharp at room temperature also become broad and diffuse at higher temperature and extend roughly over some 20 wave-numbers at 200° C. On account of this considerable broadening it is difficult to say with any degree of precision whether there is a change in frequency or not. In the case of the totally symmetric vibration which is ordinarily about 10 wave-numbers broad with an intensity maximum at 459 cm.$^{-1}$ and shading off in intensity towards the side of the exciting line, the observed changes are of a somewhat different nature. It is slightly more diffuse at the higher temperature, and shows a definite though small diminution in frequency (about 2 to 3 wave-numbers) on careful examination with a comparison iron arc.

(*b*) *Intensity Changes.*—When we pass on from considerations of frequency and structural changes to changes in intensity undergone by the Raman lines on heating the liquid, the problem is one of much greater difficulty. In this connection, we have to bear in mind a fundamental difference between liquids, on the one hand and crystalline solids like quartz, calcite, etc., on the other. The expansion of liquids at high temperatures is very large, and gives rise to an appreciable diminution in the density and refractive index of the scattering medium. In making comparative estimates of the intensity of a Raman line at two different temperatures, we have to allow for these two factors ; while the diminution in the density of liquid due to expansion causes a decrease in the number of effective scattering centres per unit volume, the change in the refractive index profoundly modifies the path of the light beam traversing the medium. It is therefore obvious that alone for these two reasons, the conditions of exposure cannot be identical at the lower and the higher temperatures. Fluctuations in the intensity of the light source during the exposure and broadening of the line under consideration at the higher temperature are two other disturbing factors in the accurate estimation of the intensity of a Raman line at two different temperatures.

In the course of his experimental work the author has found that the last-mentioned difficulty can be easily overcome and the integrated intensity

of a Raman line can be readily obtained by the simple device of using a wide slit to photograph the Raman spectrum. This procedure also effects a considerable saving in the time of exposure, so that errors consequent on fluctuations in the source intensity can be better guarded against. Thus it was found that whereas a few hours were required to photograph the Raman spectrum of CCl_4 with reasonable intensity using a narrow slit (·04 mm.), a few minutes were sufficient when a wide slit as employed (about 0·6 mm.). In working with the wide slit, however, care should be taken to see that there is no overlapping between adjacent Raman lines. It might be pointed out in this connection that in the work of Landsberg and Mandelstamm already referred to, the time of exposure at the lower and higher temperatures was 5 days and some difficulty was experienced in assessing the integrated intensity of the Raman line in question at the two different temperatures on account of its slight broadening at the higher temperature.

The errors consequent on the expansion of the liquid are not capable of being eliminated in any simple manner, and it would seem that the only way of allowing for it is to choose the Rayleigh scattering as the standard of comparison at the higher and lower temperatures. This would involve a preliminary experiment in which the Rayleigh scattering of the liquid is investigated as a function of temperature by the well-known experimental technique. Unfortunately, for want of time, it has not been possible for the author to carry out this part of the work in the case of liquid CCl_4. However, qualitative observations which can only be regarded as preliminary, appear to show that there is hardly any perceptible increase in the intensity of the stokes lines of CCl_4—perhaps even a decrease in intensity—with rise of temperature.

5. *Some General Remarks.*

(*a*) *Rotational Broadening of the Degenerate Vibrations.*—Degenerate vibrations are associated with simultaneous changes in the vibrational and rotational quantum numbers of the molecule so that they are always accompanied by rotational structure which is seldom resolved. Consequently, such vibrational lines are generally somewhat broad and diffuse and exhibit the limiting depolarisation value of 6/7 in Raman effect. Since more and more of the higher rotational levels are occupied at the higher temperatures, the rapidly increasing broadening of the degenerate vibrations on heating the liquid becomes quite intelligible.

(*b*) *Effect of Anharmonicity of the Nuclear Vibrations.*—At temperature T, the probability of a molecule existing in the vibrational state v_j is proportional to $e^{-(v_j + \frac{1}{2})\left(\frac{h\nu_j}{kT}\right)}$, where ν_j = the vibrational frequency. Hence, if we denote by N_0, N_1, N_2, · · · · the probable number of molecules in the vibrational states 0, 1, 2 · · · we have for $\nu_j = 459$ cm.$^{-1}$ (the totally symmetric vibration of CCl_4), the following percentage distribution of the molecules between various vibrational states at 25° C. and 200° C. respectively.

TABLE I.

Temp.	N_0	N_1	N_2	N_3	N_4
25° C.	89	9·8	1·07	0·11%	..
200° C.	75·36	18·46	4·67	1·13	0·35%

If we denote by I_0, I_1, I_2 · · · the contribution to the total intensity arising from the transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ · · · · and if $I = I_0 + I_1 + I_2 +$ · · · then, since $I_{v_j} \propto (v_j + 1)\, N_{v_j}$, we have,

TABLE II.

Temp.	I_0	I_1	I_2	I_3	I_4	I
25° C.	89	19·6	3·21	0·44	..	112·25
200° C.	75·36	36·92	14·01	4·52	1·75	132·56

Hence

$$\frac{I_{200^\circ}}{I_{25^\circ}} = \frac{132 \cdot 56}{112 \cdot 25} = 1 \cdot 18 : 1.$$

Thus according to Placzek's theory the integrated intensity of the totally symmetric vibrational Raman line of CCl_4 at 200°C. should be 1·18 times its intensity at 25° C.

It has been already pointed out that the effect of anharmonicity of the nuclear vibration is not explicitly taken into account in Placzek's theory. Consequently, the frequencis arising from the transition $0 \rightarrow 1$, $1 \rightarrow 2$, etc., are assumed to be exactly superposable. We know, however, that the vibrational levels of a molecule approach each other more and more with increasing quantum numbers, so that the frequency arising from the transition $v_j \rightarrow v_j + 1$ diminishes with increasing v_j. Thus for the molecule of

chlorine in the ground state, band spectroscopic data shows that $\nu\ (0 \rightarrow 1) = 557$ cm.$^{-1}$, and $\nu\,(1 \rightarrow 2) = 549$ cm.$^{-1}$ The frequency observed in the Raman spectrum of liquid chlorine is 555 cm.$^{-1}$ and corresponds to the transition $0 \rightarrow 1$. Now in the case of CCl_4 at room temperature, as we see from Tables I and II, the major contribution to the intensity of the line ν_1 (about 80%) comes from the transition $0 \rightarrow 1$, while at 200° C. the contribution from this transition is much less (about 56%) and the contribution from the transition $1 \rightarrow 2$, $2 \rightarrow 3$, · · · ·become correspondingly more important. Since these contributions are not strictly superposable we readily understand the increased diffuseness and the shift in the intensity maximum of the totally symmetric vibration at the higher temperature.

Again we saw in Section 2 that the intensity of a Raman line is determined by the value of $\left(\frac{\partial \alpha}{\partial q}\right)_0$ for the vibration concerned and that this quantity is a function of the internuclear distance of the molecule, diminishing very rapidly with increasing nuclear separation. It is well known that the effect of vibration in the case of a di-atomic molecule is to increase the average distance between the nuclei since these are a greater proportion of the time at $R > R_0$ than at $R < R_0$, the potential energy curve (V, R) being steeper to the left than to the right of the minimum. The centrifugal forces due to the rotation of the molecule also tend to increase the average distance of the nuclei. Now, the effect of increasing the temperature is to excite the higher rotational and vibrational states of the molecule and hence to increase the mean internuclear distance. As the contribution towards the intensity of the total Raman scattering from transitions involving higher quantum numbers becomes more and more important with increasing temperature in the case of relatively low Raman frequencies, it appears probable that in such cases the effect of the anharmonicity of the nuclear vibration and the centrifugal stretching due to rotation of the molecule, is to tend to cause a diminution in the intensity of such Raman lines.

In conclusion, the author's respectful thanks are due to Prof. Sir C. V. Raman for his kind interest and suggestions during the course of this work.

6. *Summary.*

After a brief review of Placzek's theory of the Raman effect, the paper gives a short account of the experimental investigations that have been hitherto carried out to verify the intensity relationships predicted by the theory. The latter indicates that (i) the ratio of the intensities of the stokes and the anti-stokes components tend to approach more and more

towards unity with increasing temperatures, and (ii) that the absolute intensities of both the stokes and the anti-stokes lines increases with increasing temperature. While theory and experiment have been found to be in conformity as regards (i), considerable discrepancies have been noticed in respect of (ii). In the case of crystalline solids like quartz, calcite, etc., previous work shows that the stokes lines instead of showing the expected rise in intensity, exhibit a pronounced weakening at higher temperatures. In this connection, the Raman spectrum of liquid CCl_4 has been investigated over an interval of temperature extending from 25° to 200° C. and the spectral changes noticed are discussed. The degenerate vibrations manifest considerable broadening at higher temperatures, the doublet at (762–790) cm.$^{-1}$, well resolved at the lower temperature, appearing as a single broad and diffuse band in the spectrum photographed at 200° C. The totally symmetric vibrational Raman line at 459 cm.$^{-1}$ is also somewhat more diffuse at the higher temperatures and shows a small diminution in frequency. The integrated intensities of the stokes lines of CCl_4 seem to show no increase at the higher temperature. It is suggested that the effect of anharmonicity of the nuclear vibrations and the centrifugal stretching of the molecule due to rotation, is probably responsible for this departure from the expected increase in intensity.

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EFFECT OF OBLIQUE REFRACTION AT THE PRISM SURFACES ON THE RELATIVE INTENSITIES OF RAMAN LINES.

By Dr. A. Veerabhadra Rao.

(From the Department of Physics, Andhra University, Waltair.)

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1. Introduction.

The depolarisation introduced by oblique refraction of light through the prisms of a glass spectrograph and its effect on the polarisation measurements in Raman spectra are very well known to workers in the field. But, till now, the very important part played by this in the intensity measurements of Raman lines has somehow escaped their attention. It is the purpose of this paper to show how the relative intensities of Raman lines are considerably modified on account of this phenomenon.

2. Experimental Technique.

The experimental procedure usually employed for the measurement of the relative intensities of Raman lines is briefly the following. Light scattered from the Raman tube which is illuminated by a mercury arc placed either vertically above or on the side in conjunction with or without a condenser, is focussed on the slit of the spectrograph. The spectrum is photographed on a photographic plate on which are also recorded a set of graded intensity marks given either by the method of varying slit widths or by the help of step-filter. The continuous radiation employed for the purpose is generally the light emitted by a tungsten ribbon lamp, the characters of which are known.

The different Raman lines with the corresponding regions of the intensity marks are microphotometered and their intensities are computed with reference to the intensity marks. Taking into consideration the known distribution of intensity in the intensity marks, it is a matter of simple calculation to get the relative intensities of the various lines.

It is apparent from the above procedure that no account is taken of the influence of the instrument on the intensities of the various lines. We

tacitly assume that the relative intensities of the various lines remain unaltered by their passage through the spectrograph. Such an assumption is correct only if all the lines under comparison are depolarised to the same degree. Otherwise it is obviously wrong. We shall examine this question in greater detail.

3. *'The Instrument Error.'*

Applying the theory of refraction to the case of passage of light through a prism, it can easily be shown that light polarised with its electric vector parallel to the refracting face of the prism is transmitted to a lesser extent than light polarised with its electric vector perpendicular to the refracting face. Thus if we send a beam of unpolarised light through the spectrograph it comes out as partially polarised light as the horizontal and the vertical components are weakened to different extents. In general, therefore, the state of polarisation of the incident beam is altered by passage through the instrument. We shall refer to this as 'The instrument error' and it is usually taken account of in depolarisation measurements in Raman spectra.

4. *Effect of the Instrument Error on the Intensities of Raman Lines.*

Let us examine how this instrument error effects the relative intensities. Consider a Raman tube illuminated from the side. Let us confine our attention to two lines a and b of intensities I_a and I_b. Let their depolarisation factors, defined as the ratio of the parallel to the perpendicular components with respect to the direction of illumination, be ρ_a and ρ_b. For the case of illumination from the side the parallel component will have its electric vector vibrating in the horizontal direction and hence will have a component perpendicular to the refracting face of the prism while the perpendicular component will have its electric vector vibrating vertically and therefore parallel to the refracting face of the prism. If we split up these lines a and b into their respective horizontal and vertical components we have :

TABLE I.

Line	Total Intensity	$\parallel^l$ Comp.	$\perp^r$ Comp.
a	I_a	$\frac{\rho_a I_a}{1+\rho_a}$	$\frac{I_a}{1+\rho_a}$
b	I_b	$\frac{\rho_b I_b}{1+\rho_b}$	$\frac{I_b}{1+\rho_b}$

These different components suffer changes in their intensities due to their passage through the spectrograph. If the vertical component alters in intensity in the ratio $1 : \sigma$ due to transmission through the spectrograph relatively to the horizontal component, while the horizontal component is supposed unaffected, then σ is called the instrument correction, and the altered intensities of the various components and the total intensities of the two lines will be as given below :

TABLE II.

Line		Intensity Before transmission	Intensity After transmission
a	$\parallel^{l}$ Comp.	$\frac{\rho_a I_a}{1+\rho_a}$	$\frac{\rho_a I_a}{1+\rho_a}$
	$\perp^{r}$ Comp.	$\frac{I_a}{1+\rho_a}$	$\frac{\sigma I_a}{1+\rho_a}$
	Total	I_a	$I_a \frac{\rho_a+\sigma}{1+\rho_a}$
b	$\parallel^{l}$ Comp.	$\frac{\rho_b I_b}{1+\rho_b}$	$\frac{\rho_b I_b}{1+\rho_b}$
	$\perp^{r}$ Comp.	$\frac{I_b}{1+\rho_b}$	$\frac{\sigma I_b}{1+\rho_b}$
	Total	I_b	$I_b \frac{\rho_b+\sigma}{1+\rho_b}$

Thus we see that the relative intensities of the two lines a and b change from $\frac{I_a}{I_b}$ to $\frac{I_a}{I_b} \cdot \frac{(\rho_a+\sigma)(1+\rho_b)}{(\rho_b+\sigma)(1+\rho_a)}$ after transmission, or denoting the altered intensities by dashed letters we have

$$\frac{I_a'}{I_b'} = \frac{I_a}{I_b} \cdot \frac{(\rho_a+\sigma)(1+\rho_b)}{(\rho_b+\sigma)(1+\rho_a)}.$$

The magnitude of the change in the relative intensity depends, therefore, on the individual depolarisations of the lines and on the magnitude of the instrument error. The above equation shows that if we start with two lines of

the same depolarisation value, *i.e.*, $\rho_a = \rho_b$, then $\frac{I_a'}{I_b'} = \frac{I_a}{I_b}$ or there is no change in the relative intensities of equally depolarised lines. Also when $\sigma = 1$ we have $\frac{I_a'}{I_b'} = \frac{I_a}{I_b}$. But such a case never arises because it would mean that the prism is able to transmit the two components equally which is possible only when the beam enters and leaves the prism normal to the surface.

To appreciate the magnitude of the change let us take an extreme case where one of the lines is perfectly polarised ($\rho_a = 0$) and the other depolarised to the limit ($\rho_b = 6/7$). Then working with a spectrograph whose 'instrument correction' is σ, we have

$$\frac{I_a'}{I_b'} = \frac{I_a}{I_b} \cdot \frac{(0 + \sigma)\left(1 + \frac{6}{7}\right)}{\left(\frac{6}{7} + \sigma\right)(1 + 0)} = \frac{13\sigma}{6 + 7\sigma} \cdot \frac{I_a}{I_b}.$$

For an instrument with σ equal to 0·5,* we have

$$\frac{I_a'}{I_b'} \simeq 0{\cdot}7 \ \frac{I_a}{I_b}.$$

Since the value of σ is always less than 1, $\frac{I_a'}{I_b'}$ is always less than $\frac{I_a}{I_b}$. The well polarised lines, therefore, always suffer a greater loss of intensity than the unpolarised lines due to their passage through the spectrograph under the above conditions of experiment.

5. Effect of Direction of Illumination on the Intensities of Raman Lines.

A very important corollary comes out of the above considerations. As already mentioned in Section 2, the direction of illumination can either be horizontal when the Raman tube is illuminated from the side, or vertical when the arc is situated above the Raman tube. Both methods are in vogue. In the previous section we have dealt with the former type of illumination. In the alternative method of illumination, it is the parallel component which is now vertical that has its electric vector parallel to the refracting face while the perpendicular component which is horizontal has a component perpendicular to the refracting face. If we consider the line *a*, the component that suffers a relatively greater loss of intensity in the present case will be the parallel component. Treating the line *b* also similarly and working out just as we have done in the former case, we arrive at results tabulated below.

* Such values are frequently met with in spectrographs.

TABLE III.

Line		Intensity Before transmission	Intensity After transmission
a	$\perp^r$ Comp.	$\frac{I_a}{1+\rho_a}$	$\frac{I_a}{1+\rho_a}$
	$\parallel^l$ Comp.	$\frac{\rho_a I_a}{1+\rho_a}$	$\frac{\sigma \rho_a I_a}{1+\rho_a}$
	Total	I_a	$I_a \cdot \frac{1+\sigma\rho_a}{1+\rho_a}$
b	$\perp^r$ Comp.	$\frac{I_b}{1+\rho_b}$	$\frac{I_b}{1+\rho_b}$
	$\parallel^l$ Comp.	$\frac{\rho_b I_b}{1+\rho_b}$	$\frac{\sigma \rho_b I_b}{1+\rho_b}$
	Total	I_b	$I_b \cdot \frac{1+\sigma\rho_b}{1+\rho_b}$

$$\therefore \frac{I_a'}{I_b'} = \frac{I_a}{I_b} \cdot \frac{(1+\sigma\rho_a)(1+\rho_b)}{(1+\sigma\rho_b)(1+\rho_a)}.$$

In this case also if $\rho_a = \rho_b$ or if $\sigma = 1$

$$I_a'/I_b' \text{ is equal to } I_a/I_b.$$

Taking the extreme case as before with $\rho_a = 0$ and $\rho_b = 6/7$

$$\frac{I_a'}{I_b'} = \frac{I_a}{I_b} \cdot \frac{(1+\sigma\times 0)(1+\frac{6}{7})}{(1+\sigma\times\frac{6}{7})(1+0)} = \frac{13}{7+6\sigma} \cdot \frac{I_a}{I_b}.$$

$$\text{If } \sigma = 0{\cdot}5, \frac{I_a'}{I_b'} \simeq 1{\cdot}3 \frac{I_a}{I_b}.$$

As σ is always less than unity, we have $\frac{I_a'}{I_b'}$ always greater than $\frac{I_a}{I_b}$. Thus when the Raman tube is illuminated from above, the intensity of a well-polarised line is apparently enhanced relative to the unpolarised lines.

By comparing this with the previous result we note the very interesting fact, that by merely changing the direction of illumination of the Raman tube from the horizontal to the vertical, the observed intensity of a completely

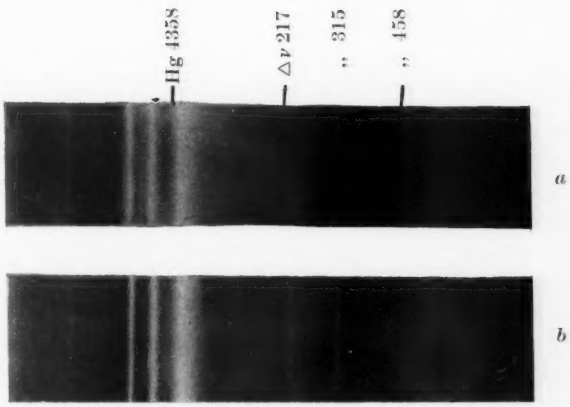

FIG. 1.

Raman Spectrum of CCl_4.

a—Illumination from the top.

b— ,, ,, the side.

polarised line is enhanced in the ratio $\frac{6+7\sigma}{7+6\sigma} \cdot \frac{1}{\sigma}$ for a given intensity of a completely depolarised line. It is as much as a doubling of intensity when we are working with an instrument for which σ is nearly equal to 0·5.

The accompanying picture which is the Raman spectrum of CCl_4 taken with a glass-Littrow-Spectrograph, shows clearly the effect of the change of direction of incidence. Fig. 1 (*a*) represents the appearance of the Raman lines $\Delta\nu$ 217, 315, 458 of depolarisations nearly 0·85, 0·85 and 0·05 respectively when the liquid tube is illuminated from the top while Fig. 1 (*b*) shows the appearance of the lines when the Raman tube is illuminated from the side. In (*a*) the well-polarised Raman line 458 appears to be more intense than the other two depolarised lines while in (*b*) it is definitely less intense.

Incidentally, it may be mentioned that large discrepancies between the results reported by various workers* in regard to the relative intensities of these lines are to be explained in the above manner as it is likely that different workers may have adopted different methods of illumination. All the relative intensities hitherto reported in respect of Raman lines are therefore to be regarded as incorrect except in such cases where the lines under question are all depolarised to the same extent. In arriving at the correct values, the different degrees of polarisation of the various lines and the 'instrument error' have to be taken into account. In certain typical cases such as CCl_4 and C_6H_6 this procedure is being adopted and the results will be reported in due course.

6. *Summary.*

The effect of the polarisation introduced by oblique refraction at the prism faces in a spectrograph on the relative intensities of Raman lines is discussed. It is shown that if illumination from the side is adopted, the intensity of the well-polarised lines is apparently diminished in relation to the unpolarised ones and the reverse if illumination from the top is adopted. A particularly striking illustration is provided in the Raman spectrum of carbon tetrachloride.

In conclusion, the author wishes to record his best thanks to Mr. S. Bhagavantam for his helpful criticism and deep interest in this work.

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* P. Daure, *Ann. de Phys.*, 1929, **12**, 375.
A. Carelli and J. J. Went, *Zeit. f. Phys.*, 1932, **76**, 236.
J. T. Dhar, *Ind. Jour. Phys.*, 1934, **9**, 189.
A. Veerabhadra Rao, *Zeit. f. Phys.*, 1935, **97**, 154.

CHEMISTRY OF β-ARYL-GLUTACONIC ACIDS.

Part IV. c-Acetylation of β-aryl-glutaconic Anhydrides: Derivatives of α-Aceto-β-aryl-glutaconic Acids.

By G. R. Gogte, M.Sc., Ph.D.

(From the Department of Organic Chemistry, Indian Institute of Science, Bangalore.)

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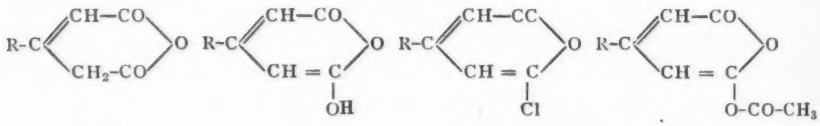
It is well known that the anhydrides of glutaconic acids differ as a class from the anhydrides of dibasic acids in titrating as monobasic acids and giving colourations with ferric chloride. Thole and Thorpe[1] explained this peculiarity by the hydroxy anhydride formula (II) based upon the idea of the wandering of the mobile hydrogen atom out of the three carbon sytem of the glutaconic anhydrides (I) to the neighbouring carbonyl group. This theory received support from the observation that the αα-dimethyl-glutaconic anhydride, which does not contain any mobile hydrogen atom, behaved normally.[2] It is noteworthy, however, that with the exception of the αβ-dimethyl-glutaconic anhydride, no neutral acetyl (IV) or benzoyl derivatives of any glutaconic anhydride have been described, although neutral chloro-anhydrides (III) were known.



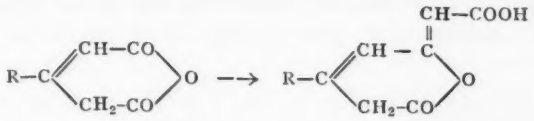
(I) (II) (III) (IV)

In attempting to prepare such neutral acetyl derivatives from the β-aryl-glutaconic anhydrides by the action of acetic anhydride and fused sodium acetate, the present author had isolated compounds indicating condensation with one molecule of acetic acid. These compounds, however, titrate as monobasic acids, give colouration with ferric chloride and by the action of strong alkalis, yield neutral compounds instead of the original glutaconic acids, and hence the constitution of glutaconyl-acetic acid was suggested

[1] *J.C.S.*, 1911, **99**, 2211.

[2] Henrich, *Monatsh*, 1899, 20, 560 ; Perkin and Smith, *J.C.S.*, 1903, **83**, 8.

for them.[3] Limaye and Bhave examined this reaction extensively and proved that it proceeded according to the Perkin's reaction.[4]



(I) (V)

On attempting the Einhorn's method[5] for acetylating the β-aryl-glutaconic anhydrides, it being known to give *o*-acetyl-derivatives,[6] actually products were obtained which have been found identical with those resulting from the action of acetic anhydride and fused sodium acetate. In the present paper, it has been shown that these derivatives are not glutaconyl-acetic acids (V) as described by Limaye and Bhave,[4] but they are *c*-acetyl-glutaconic anhydrides (VI). The three typical cases investigated in the present paper are: the β-(4-methoxy-phenyl)-glutaconic anhydride,[7] the β-(2-methoxy-5-methyl-phenyl)-glutaconic anhydride[8] and the β-(4-methoxy-3-methyl-phenyl)-glutaconic anhydride.[9]

In the example of the β-(4-methoxy-phenyl)-glutaconic anhydride, for instance, both the above methods of acetylation lead to the formation of a product, m.p. 132° C. The formation of this product by the action of pyridine and acetyl-chloride-(Einhorn's method)—would indicate that it is not a glutaconyl acetic acid but, in all probability, it is an acetyl derivative of the glutaconic anhydride (I). This conclusion is supported by the following observations. The action of dilute hydrochloric acid on the product, m.p. 132° C., produced the β-(4-methoxy-phenyl)-propylene[10] (VIII). This compound is known to result from the original glutaconic acid[7] (VII) or its anhydride (I) by the action of the same reagent. The formation of the propylene derivative in the present case is thus evidently through the intermediate glutaconic anhydride (I), which latter results from the product, m.p. 132° C., by the removal of an acetyl group by the action of hydrochloric acid. Secondly, aniline has been found to react with the product, m.p.

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[3] Gogte, *Bomb. Univ. M.Sc. Thesis*, 1931, p. 18 ; *Proc. Ind. Sci. Congress*, 1934, p. 230.

[4] Limaye and Bhave, *J. Univ. Bomb.*, 1933, **2**, Part II, 82.

[5] Einhorn and Holland, *Annalen*, 1893, **301**, 95.

[6] Claison and Haase, *Ber.*, 1900, **33**, 1242.

[7] Limaye and Bhave, *J. Ind. C. S.*, 1931, **8**, 137.

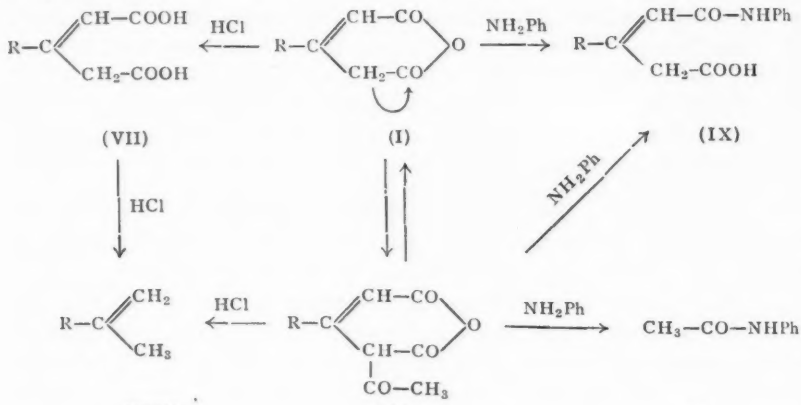
[8] Gogte, *Proc. Ind. Acad. Sci.*, (A), 1934, **1**, 53.

[9] Dixit, *J. Ind. C. S.*, 1931, **8**, 787.

[10] Behal and Tiffenau, *Compt. Rend.*, 1901, **132**, 561.

132° C., when warmed in benzene solution, to give the β-(4-methoxy-phenyl)-glutaconic acid-semianilide[7] (IX) and acetanilide (X). This semianilide is thus evidently formed by the further action of aniline on the β-(4-methoxy-phenyl)-glutaconic anhydride (I) which is formed as the primary product of the reaction.

As already observed, the action of alkali on the acetyl-glutaconic anhydride, m.p. 132° C., results in the formation of *p*-methoxy-aceto-phenone and a kentoic acid and not the original glutaconic acid.[4] This observation coupled with the titratibility and colouration with ferric chloride sets aside an *o*-acetyl structure (IV), and hence the product is a *c*-acetyl-glutaconic anhydride (VI).

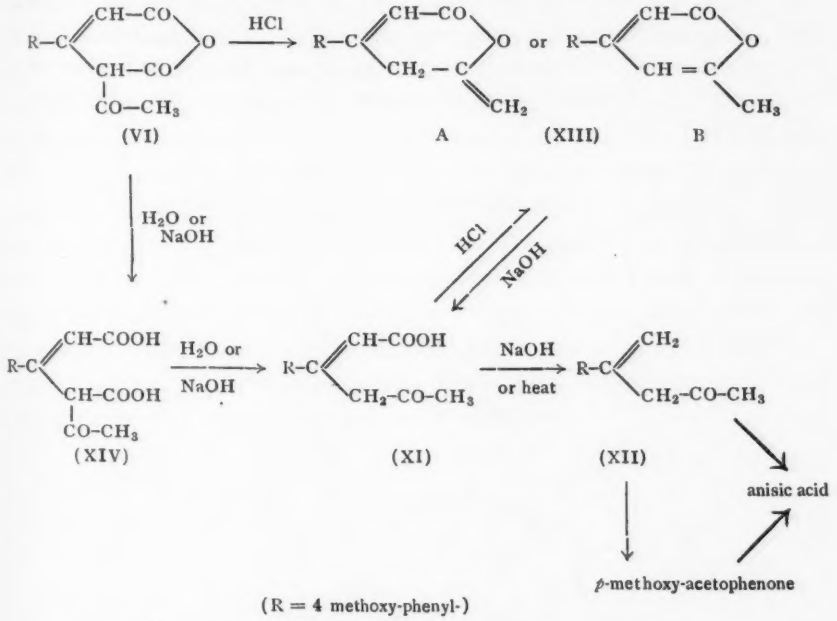


Here, by substituting a CH_3-CO-group on the carbon atom containing the tautomeric hydrogen atom of the glutaconic anhydride, the mobility of that hydrogen gets enhanced, and as this mobility is responsible for the acidity and $FeCl_3$ colouration, the *c*-acetyl-glutaconic anhydride (VI) titrates as a strong acid and gives colouration with ferric chloride, and in this respect can be compared with the *c*-acetyl-aceto-acetic ester or the *c*-acetyl-dimethyl-dihydro-resorcinol.[11]

The anhydride nature of the *c*-acetyl-glutaconic anhydride (VI) is further confirmed by the observation that, when acted upon even by water, it produced the same ketonic acid (m.p. 125° C.) obtained by Limaye and

[11] James, *Annalen*, **226**, 210 ; Claisen, *ibid.*, **277**, 171 ; Crossley and Renouf, *J.C.S.*, 1912, **101**, 1524.

Bhave[4] by the action of caustic alkali. On the basis of the constitution (VI), this ketonic acid (XI) is formed by the addition of water giving rise to the unstable compound (XIV) and subsequent removal of carbon dioxide from the latter. This constitution also explains the reduction of the ketonic acid to the β-(4-methoxy-phenyl)-γ-aceto-butyric acid[12] as observed by Limaye and Bhave.[4] It has been found that the ketonic acid (XI) gets decarboxylated even by refluxing with caustic alkalis to produce the neutral ketone, m.p. 48° C. (XII), which has been found to give the known *p*-methoxy-acetophenone by further action of caustic alkali. It is not possible to oxidise the ketone (XII) to the *p*-methoxy-β-methyl-cinnamic acid according to the procedure of Limaye and Bhave.[4] On oxidation with alkaline hypobromite both this ketone (XII) as well as the *p*-methoxy-aceto-phenone produced anisic acid. These reactions explain the formation of *p*-methoxy-acetophenone from the *c*-acetyl-glutaconic anhydride (VI) by the action of caustic alkalis.



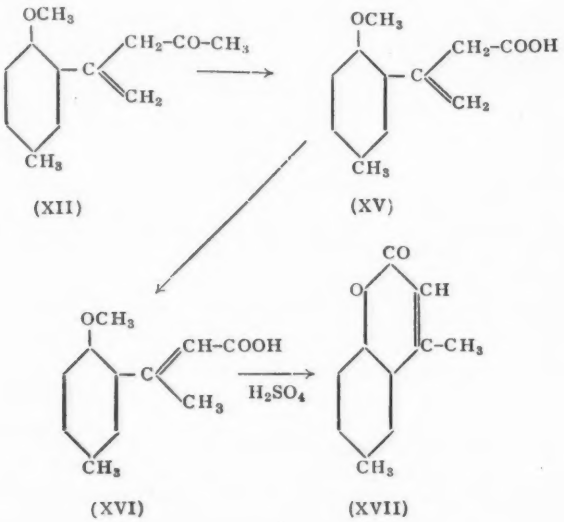
(R = 4 methoxy-phenyl-)

The ketonic acid (XI) gets transformed quantitatively into a lactone, m.p. 112° C. (XIII), by the action of hydrochloric acid. Limaye and Bhave[4]

[12] Vorlander, *Annalen*, 1891, **294**, 253.

state that they have obtained this lactone in 40% yield from the product m.p. 132° C. [the *c*-acetyl-anhydride (VI)] by the action of hydrochloric acid, and this they have used as an argument in favour of the glutaconyl-acetic acid structure (V). It is, however, found that the action of concentrated hydrochloric acid on the *c*-acetyl-glutaconic anhydride (VI) results in the formation of the lactone (XIII) only in 5% yield, the rest being a high boiling oil. The formation of the lactone (XIII) from the *c*-acetyl-anhydride (VI) is readily explained when it is remembered that compound (VI) gives the ketonic acid (XI) merely on treatment with water, and the latter gets converted into the lactone (XIII) by the action of hydrochloric acid.

When R = 2-methoxy-5-methyl-phenyl- in the above scheme, the action of alkali on the *c*-acetyl-anhydride (VI) stops with the production of the ketone (XII). On oxidation with hypobromite, this ketone gives an acid (XV) which being a $\beta\gamma$-unsaturated acid gets immediately transformed into the 2-methoxy-5-methyl-β-methyl-cinnamic acid (XVI), and this latter gives the 4 : 6-dimethyl-coumarin[13] by the action of sulphuric acid. Such wandering of a $\beta\gamma$-double bond of unsaturated acids to the $\alpha\beta$-position is well known.[14]



[13] Pechmann and Cohen, *Ber.*, 17, 2187.

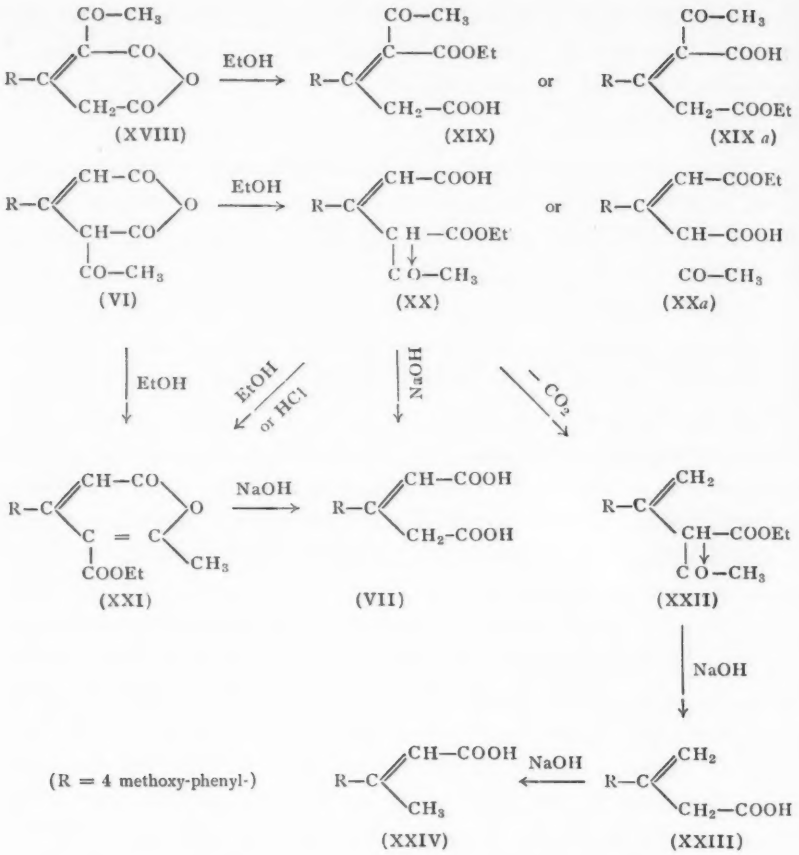
[14] Fittig, *ibid.*, 1891, 24, 82.

The decarboxylation of the ketonic acids (XI) by caustic alkalis to produce the ketones (XII) becomes intelligible by applying the principle of Vinylogy,[15] according to which the ketonic acids are vinylogs of aceto-acetic acid and have similar properties.

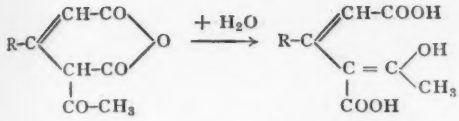
All these above reactions could also be accounted for by the alternative structure (XVIII) for the *c*-acetyl-glutaconic anhydrides. The action of alcohol or (VI) or (XVIII) can give rise to the acid esters (XIX), (XIX *a*) (XX), (XX *a*). Of these four formula (XIX *a*) or (XX *a*) can be rejected as they represent unstable β-ketonic acids. Of the remaining (XIX) and (XX) only the latter contains a tautomeric hydrogen atom. The acid-ester (m.p. 138° C.), obtained by the action of alcohol on the *c*-acetyl-anhydride (m.p. 132° C.), as well as its decarboxylation product have been actually found to give pronounced colourations with ferric chloride. The acid-ester gives a lactonic ester, m.p. 106° C. (XXI) by the action of hydrochloric acid. This lactonic ester is formed even by the action of alcohol on the acid-ester, and thus is also obtained along with the acid-ester in the original reaction. All these clearly point to the existence of a reactive tautomeric hydrogen atom in the acid-ester. Hence the acid-ester has the structure (XX) and consequently the *c*-acetyl-glutaconic anhydride has the structure (VI). These constitutions (XX), (XXI), (XXII) for the acid-ester, the lactonic ester and the decarboxylation product respectively are further supported by the fact that, by the action of caustic alkalis, the acid-ester and the lactonic ester gave the β-(4-methoxy-phenyl)-glutaconic acid[7] (VII), and the decarboxylation product produced the *p*-methoxy-β-methyl-cinnamic acid[1] (XXIV), evidently through the intermediate acid[16] (XXIII).

[15] Fuson, *Chem. Reviews*, 1935, **16**, 1.

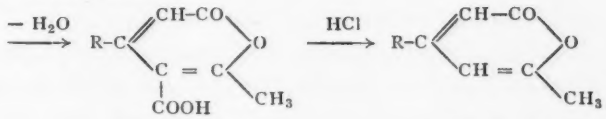
[16] Schrœter, *Ber.*, 1908, **41**, 9.



By the action of 90% sulphuric acid, the *c*-acetyl anhydride, m.p. 132° C. (VI) gets transformed into an isomeric acid, m.p. 181° C., which also gives the ketonic acid (XI) and *p*-methoxy-aceto-phenone by the action of caustic alkali. By the action of hydrochloric acid, however, this acid (m.p. 181° C.) produces only the lactone (XIII). This acid could be esterified only through its silver salt, and its ethyl ester has been found identical with the lactonic ester (XXI) described above. Hence the acid (m.p. 181° C,) is evidently formed through the intermediate unstable acid (XIV) as a result of the addition and subsequent removal of a molecule of water from the *c*-acetyl anhydride (VI), and it is ascribed the structure (XXV). The intra-molecular change is represented as follows :



(VI) (XIV enrol form)



(XXV) (XIII B)

(R = 4 methoxy-phenyl-)

and is thus analogous to the action of alcohol on the *c*-acetyl anhydride. Consequently, the lactone possesses the structure (XIII B) and not (XIII A). The formation of the ketonic acid (XI) and *p*-methoxy-aceto-phenone takes place evidently through the intermediate acid (XIV) in the way described before. This intra-molecular change takes place also in compound (VI) when R = 2-methoxy-5-methyl-phenyl.

Conclusion.

β-Aryl-glutaconic anhydrides have been found to get acetylated by acetyl chloride in the presence of pyridine or by acetic anhydride in the presence of fused sodium acetate. The acetylation products have been proved to be *c*-acetyl-glutaconic anhydrides, the acetyl group being attached to the methylene carbon atom of the glutaconic anhydride. In view of the fact that acetylation by pyridine and acetyl chloride is known generally to lead to the formation only of *o*-acetyl-derivatives, the case of β-aryl-glutaconic anhydrides seems to be remarkable.

Experimental.

Acetylation of β-(4-methoxy phenyl)-glutaconic anhydride: Formation of α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride (VI).—The glutaconic anhydride—crystallised freshly from benzene—(20 g.) was dissolved in freshly distilled pyridine (50 c.c.), the solution cooled in ice and acetyl chloride (7 g.) was slowly added with shaking. After the vigorous reaction subsided, the reaction mixture was allowed to attain the room temperature and then warmed a while on a water-bath and kept for three hours at the room temperature. It was poured in excess of ice-cooled dilute hydrochloric acid and kept overnight. The aqueous portion was decanted off, the residual oily product washed with water and rubbed with ether and the acetyl derivative

which separated as a granular solid, was crystallised from ethyl acetates in light plates, m.p. 132° C. (Found : Eq. = 262 ; C = 64·5% ; H = 4·5% ; $C_{14}H_{12}O_5$ requires Eq. = 260 ; C = 64·6% ; H = 4·6%.) The compound is very soluble in acetone and benzene and sparingly in alcohol, ethyl acetate or chloroform. The compound yields an insoluble sodium salt when treated even with N/5 sodium hydroxide solution.

Synthesis of the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride by the action of sodium acetate and acetic anhydride on the β-(4-methoxy-phenyl)-glutaconic acid.—(Improved method ; *cf.* Limaye and Bhave.) The glutaconic acid (20 g.) and freshly fused sodium acetate (25 g.) were ground together in a mortar and heated on a boiling water-bath with acetic anhydride (30 c.c.) for ten minutes with shaking. The dark red solution was poured in water (400 c.c.) and after standing for ½ hour, the clear red solution was filtered and acidified with conc. hydrochloric acid (30 c.c.). The sticky red precipitate became granular on keeping for an hour. It was filtered, washed with cold alcohol and crystallised from ethyl acetate ; yield 17 g.

Action of hydrochloric acid on the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride : Formation of the known β-(4-methoxy-phenyl)-propylene (VIII). —The *c*-acetyl anhydride (2 g.) was finely powdered and refluxed with 20% hydrochloric acid (20 c.c.) for 5 minutes, and the resulting oily product subjected to steam distillation, when the propylene derivative came out as a colourless solid, m.p. 32° C.

Action of concentrated hydrochloric acid (*cf.* Limaye and Bhave).—The *c*-acetyl-anhydride (2 g.) was refluxed with conc. hydrochloric acid (5 c.c.) for 1½ hours and the whole poured in water. The oily substance which separated was extracted with ether, the ether solution washed with sodium carbonate solution and water, dried, and the ether removed in a vacuum desiccator when a small amount of a crystalline body accompanied by much of an oil was obtained. The oil was removed on a porous plate and the substance was crystallised from methyl alcohol in colourless glistening light plates, m.p. 112° C. (yield 0·1 g.). This compound is identical with the lactone (XIII).

Action of aniline on the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride : Formation of the β-(4-methoxy-phenyl)-glutaconic acid-semianilide and acetanilide.—The *c*-acetyl anhydride (2 g.) was dissolved in benzene (5 c.c.) and aniline (1·5 g.) was added. On just boiling the solution a vigorous reaction took place and the glutaconic semianilide (IX) separated as a colourless precipitate. It was filtered and crystallised from alcohol in light colourless needles, m.p. 186° C. (decomp.).

The benzene filtrates in the above were concentrated, removing the last traces of benzene in a vacuum, and the residue treated with hot sodium carbonate solution. On filtering and keeping overnight, the acetanilide (X) separated as colourless crystals. It was filtered, washed and crystallised from water in colourless plates, m.p. 114° C.

Action of alkali on the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride: *Formation of* p-*methoxy-β-acetonyl-cinnamic acid* (*XI*).—The acetyl anhydride (5 g.) was mixed with N-sodium hydroxide solution (100 c.c.) and warmed on a water-bath until the insoluble sodium salt just disappeared. The clear orange solution was kept at the room temperature for 5 hours, cooled in ice and acidified with dilute hydrochloric acid. The oily acids were extracted with ether, the ether extract washed with water and extracted with 10% sodium carbonate solution. This sodium carbonate extract was washed with ether, the ether removed by bubbling air, cooled in ice and acidified. An oily acid separated which solidified by rubbing and keeping with water for an hour. It was filtered, dried and crystallised from ethyl acetate in colourless prismatic needles, m.p. 125° C. (decomp). This acid is also obtained by the action of water on the *c*-acetyl anhydride thus:—The *c*-acetyl anhydride (5 g.) was finely powdered and refluxed with distilled water (250 c.c.) for 15 minutes when it changed into an oily body. The aqueous solution was decanted off and the oily body again treated with water as above. The aqueous portions were filtered on cotton wool and kept overnight when the substituted cinnamic acid crystallised out. It was filtered and purified as above.

The *lactone* (XIII) of the above substituted cinnamic acid is better prepared by refluxing the cinnamic acid (1 g.) with hydrochloric acid (5 c.c.) for half an hour and pouring in water. On cooling, the lactone was filtered, washed with sodium carbonate solution, and crystallised from methyl alcohol in glistening colourless light plates, m.p. 112° C.

Decarboxylation of 4-methoxy-β-acetonyl-cinnamic acid: Formation of 4-methoxy-β-acetonyl-styrene (*XII*).—After decarboxylating the above substituted cinnamic acid at 130–40° C. temperature, the resulting oil was dissolved in ether, washed with sodium carbonate solution and water, the ether removed, and the residue kept in a vacuum desiccator, when it solidified. Traces of oily matter were removed on a porous plate, and the styrene on crystallisation from ether or petroleum ether melted at 50° C. and not at 48° C. as given by Limaye and Bhave. *Semicarbazone* crystallises from alcohol in colourless light plates, m.p. 188–89° C. (decomp.). This styrene

could not be oxidised to the *p*-methoxy-β-methyl cinnamic acid as stated by Limaye and Bhave.

This acetonyl styrene (XII) could also be obtained from the *c*-acetyl anhydride (VI) or the acetonyl-cinnamic acid (XI) by refluxing with 10% sodium hydroxide until an oil had just appeared (10 minutes). The styrene was identified through its semicarbazone. When the *c*-acetyl anhydride, the acetonyl-cinnamic acid or the acetonyl-styrene were refluxed with 10% sodium hydroxide solution for two hours all of them yielded the known *p*-methoxy-acetophenone (XIV), the semicarbazone of which, when crystallised from alcohol, melted at 189–90° C. (decomp.) and not at 181–82° C. as stated by Mameli (G. 39, II, 171).

Oxidation of 4-methoxy-β-acetonyl-styrene: Formation of anisic acid.—Bromine (2·5 g.) was gradually added to an ice-cooled 3-N-sodium hydroxide solution (13 c.c.) and the acetonyl-styrene—finely powdered—(1 g.) was shaken with this hypobromite solution for 8 hours. The bromoform was removed from the resulting solution by washing with ether, and the alkaline solution was saturated with sulphur dioxide gas until it was acidic. The precipitated anisic acid was crystallised from water.

The *p*-methoxy-acetophenone also gives anisic acid on oxidation with hypobromite as above. Thus in the above oxidation, a primary transformation of the acetonyl-styrene into the *p*-methoxy-acetophenone appears to take place during the oxidation.

Action of alcohol on the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride: Formation of the monoethyl-ester (XX) of α-aceto-β-(4-methoxy-phenyl)-glutaconic acid.—The *c*-acetyl-glutaconic anhydride (5 g.) was refluxed with absolute alcohol (25 c.c.) for 3 hours, the alcohol distilled off and the residue dissolved in ether. The ether solution was washed with water and extracted with 10% sodium carbonate solution. (For the working up of this ether solution after Na_2CO_3 extraction see next paragraph.) The sodium carbonate extract was washed with ether, cooled in ice-water and acidified with hydrochloric acid. The resulting oily acid solidified on decanting off the aqueous layer and rubbing repeatedly with water. It was filtered, dried and purified by dissolving in alcohol and precipitating with water. The acid-ester separated as colourless light needles, m.p. 138° C. (decomp). (Found: Eq. = 303; C = 62·6%; H = 5·8%; $C_{16}H_{18}O_6$ requires Eq. = 306; C = 62·7%; H = 5·9%.) This acid-ester gives a deep violet colouration with ferric chloride in cold alcoholic solution. When refluxed with 10% sodium-hydroxide solution for 5 minutes, this acid-ester is quantitatively converted into the

β-(4-methoxy-phenyl)-glutaconic acid (VII). The *semicarbazone* of this acid-ester crystallises from methyl alcohol in colourless light plates, m.p. 154° C. (decomp.).

The lactonic ester (XXI) from the monoethyl-ester of α-aceto-β-4-methoxy-phenyl)-glutaconic acid.—The ether solution in the above experiment, after removing the acid-ester, was again washed with sodium carbonate solution and water, dried, and the ether removed in a vacuum desiccator when the lactone separated as colourless glistening crystals, accompanied by some oil. The oil was removed by pressing between filter papers, and the lactone was crystallised from methyl alcohol in colourless parallelogramic plates, m.p. 106° C. (Found : C = 66·5% ; H = 5·5% ; $C_{16}H_{16}O_5$ requires C = 66·7% ; H = 5·6%.) This lactonic ester can be prepared quantitatively from the above acid-ester, m.p. 138° C. (XX), by refluxing with conc. hydrochloric acid for 10 minutes. This lactonic ester, on boiling with 10% sodium hydroxide, is converted into the β-(4-methoxy-phenyl)-glutaconic acid (VII). This lactonic ester does not give any colouration with ferric chloride.

Decorboxylation product (XXII) of the monoethyl-ester of the α-aceto-β-(4-methoxy-phenyl)-glutaconic acid.—The monoethyl ester (XX) was decorboxylated by heating at 150°–60° C. temperature until the evolution of carbon dioxide ceased. The resulting liquid was dissolved in ether, the ether solution was washed with sodium carbonate solution and water, dried, the ether removed and the resulting oil distilled at 189–91° C./12 mm. (Found : C = 68·6% ; H = 6·8% ; $C_{15}H_{18}O_4$ requires C = 68·7% ; H = 6·9%.) This decarboxylation product gives a violet colouration with ferric chloride. By refluxing with 10% sodium hydroxide solution for 15 minutes this decarboxylation product gives a mixture of *p*-methoxy-β-methyl-cinnamic acid (XXIV) crystallising in light rectangular plates from alcohol, m.p. 155° C., and *p*-methoxy-aceto-phenone.

Action of moist sulphuric acid on the α-aceto-β-(4-methoxy-phenyl)-glutaconic anhydride (VI) : Formation of the lactonic acid (XXV) of α-aceto-β-(4-methoxy-phenyl)-glutaconic acid (XIV).—The *c*-acetyl anhydride, m.p. 132°C. (5 g.) was dissolved in ice-cooled 90% sulphuric acid (10 c.c.) and the solution kept at room temperature for four hours. On pouring this in water and rubbing, a precipitate was formed, which was dissolved in sodium carbonate solution and precipitated by hydrochloric acid. The resulting acid was filtered, washed with water and crystallised from methyl alcohol in colourless needles, m.p. 181° C.; yield 4·5 g. (Found : Eq. = 263 ; C = 64·4% ; H = 4·5 % ; $C_{14}H_{12}O_5$ requires Eq. = 260 ; C = 64·6% ;

H = 4·6%.) The compound does not give any insoluble sodium salt and gives no colouration with ferric chloride. By the action of caustic alkali, it gives the ketonic acid, m.p. 125° C., and *p*-methoxy-acetophenone in the same manner as the *c*-acetyl anhydride. On refluxing this acid, m.p. 181° C., with hydrochloric acid for 3-4 hours, most of it was converted into the lactone, m.p. 112° C., the rest was recovered unchanged. When the silver salt of this acid is refluxed with ethyl-iodide in ethereal solution for three hours, the lactonic ester, m.p. 106° C., (XXI) results.

α-Aceto-β-(2-methoxy-5-methyl-phenyl)-glutaconic anhydride was prepared by the acetylation of the β-(2-methoxy-5-methyl-phenyl)-glutaconic anhydride—m.p. 117° C.—by both the methods. The product was crystallised first from alcohol and then from ethyl acetate in stout colourless needles, m.p. 129° C. (Found: Eq. = 276; C = 65·5%; H = 5·0%; $C_{15}H_{14}O_5$ requires Eq. = 274; C = 65·7%; H = 5·1%.) This *c*-acetyl anhydride, when steam distilled with 20% hydrochloric acid, gave the β-(2-methoxy-5-methyl-phenyl)-propylene which is a yellow oil with tarry smell; b.p. 96–98°/12 mm. (Found: C = 81·35%; H = 8·6%; $C_{11}H_{14}O$ requires C = 81·5%; H = 8·6%.) By the action of 75% sulphuric acid this *c*-acetyl anhydride is transformed into a lactonic acid (XXV) which crystallised by dissolving in methyl alcohol and precipitating by water in transparent rods, m.p. 179° C. (Found: Eq. = 276; C = 65·4%; H = 4·9%; $C_{15}H_{14}O_5$ requires Eq = 274; C = 65·7%; H = 5·1 %.)

2-Methoxy-5-methyl-β-acetonyl-cinnamic acid (*XI*) was obtained by treating the above *c*-acetyl-anhydride with N-caustic soda solution at room temperature overnight. The oily product obtained on acidification was extracted with ether, dried, the ether removed, the residue dissolved in cold benzene and the solution precipitated by petroleum ether until just turbid. On scratching and keeping overnight, the product came out in stout colourless needles, m.p. 101° C. (decomp.). The *lactone* obtained by refluxing this ketonic acid with hydrochloric acid, is an oil b.p. 212–14°/14 mm. (Found: C = 72·9%; H = 6·0%; $C_{14}H_{14}O_3$ requires C = 73·0%; H = 6·1%.)

Oxidation of 2-methoxy-5-methyl-β-acetonyl-styrene (*XII*): *Formation of 2-methoxy-5-methyl-β-methyl-cinnamic acid* (*XVI*).—The styrene was obtained from the above ketonic acid, m.p. 101° C., by decarboxylating at its melting point or by refluxing the ketonic acid or the *c*-acetyl anhydride with 20% sodium hydroxide for one hour. It is a yellow oil, b.p. 133° C./4 mm. Its *semicarbazone* crystallises from alcohol in colourless silky needles, m.p. 169° C. (decomp.). This styrene, on oxidation with alkaline hypobromite as described before in this paper, gave the substituted cinnamic acid (XVI) which

crystallised from 40% methyl alcohol in light silky needles, m.p. 111° C. (Found : Eq. = 206 ; C = 69·9% ; H = 6·8% ; $C_{12}H_{14}O_3$ requires Eq. = 206 ; C = 70·0% ; H = 6·8%.) This substituted cinnamic acid gave the above-mentioned β-(2-methoxy-5-methyl-phenyl)-propylene by decarboxylation, and when warmed with conc. sulphuric acid produced the known 4 : 6-dimethylcoumarin (XVII).

Monoethyl-ester of α-aceto-β-(2-methoxy-5-methyl-phenyl)-glutaconic acid.—The *c*-acetyl anhydride, m.p. 129° C. (5 g.), was refluxed with absolute alcohol (25 c.c.) for two hours and the solution cooled in ice. The unchanged *c*-acetyl anhydride which crystallised out was filtered and again refluxed with absolute alcohol, repeating this process until no unchanged *c*-acetyl anhydride crystallised out on cooling. The alcohol is distilled off from the combined alcoholic filtrates and the residue dissolved in ether. This ether solution was extracted with sodium carbonate solution, this extract washed with ether and acidified. The resulting mixture of acids was treated with cold methyl alcohol, the unchanged *c*-acetyl anhydride filtered out, and the methyl alcoholic solution allowed to evaporate at the room temperature. The resulting crystals were separated from the adhering oil by washing with xylene and were purified by dissolving in methyl alcohol and precipitating with water. The acid-ester came out as colourless rectangular plates, m.p. 118° C. (decomp.). (Found : Eq. = 323 ; C = 63·6% ; H = 6·15% ; $C_{17}H_{20}O_6$ requires Eq. = 320 ; C = 63·75% ; H = 6·25%.) This acid-ester gives a deep violet colouration with ferric chloride in cold alcohol, and when refluxed with 10% sodium hydroxide solution for fifteen minutes, is transformed into the β-(2-methoxy-5-methyl-phenyl)-glutaconic acid. The *semicarbazone* of the acid-ester melts at 158° C.

α-Aceto-β-(4-methoxy-3-methyl-phenyl)-glutaconic anhydride crystallised from acetic anhydride in light plates, m.p. 187° C. By steam distilling with dilute hydrochloric acid it gave β-(4-methoxy-3-methyl-phenyl)-propylene, b.p. 104–05° C./6 mm. (Found : C = 81·2% ; H = 8·5% ; $C_{11}H_{14}O$ requires C = 81·5% ; H = 8·6%.)

4-Methoxy-3-methyl-β-acetonyl-cinnamic acid crystallised from ethyl acetate in colourless rectangular plates, m.p. 139° C. (decomp.). *Semicarbazone*, m.p. 145° C. (decomp.). Lactone—colourless silky needles from 50% methyl alcohol, m.p. 91° C. *4-Methoxy-3-methyl-β-acetonyl styrene* is a greenish oil, b.p. 158° C./4 mm. These compounds are the same described by Limaye and Bhave as m.p. 146° C. ; m.p. 155° C. ; m.p. 95° C., respectively. The styrene on oxidation with alkaline hypobromite produced an acid which crystallises from methyl alcohol in colourless parallelogramic

plates melting at 193° C. and not at 145° C. as given by Limaye and Bhave.

Monoethyl-ester of α-aceto-β-(4-methoxy-3-methyl-phenyl)-glutaconic acid was obtained by refluxing the *c*-acetyl anhydride, m.p. 187° C., with absolute alcohol for six hours. By precipitating its methyl alcoholic solution with water, it crystallises in colourless parallelogramic plates, m.p. 126° C. (decomp.). It gives a blue colouration with alcoholic ferric chloride, and produces the β-(4-methoxy-3-methyl-phenyl)-glutaconic acid by boiling with 10% sodium hydroxide. (Found : Eq. = 324 ; C = 63·5% ; H = 6·1% ; $C_{17}H_{20}O_6$ requires, Eq. = 320 ; C = 63·7% ; H = 6·2%.)

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A STUDY OF THE RAMAN EFFECT IN SODIUM NITRATE.

By P. Pattabhiramayya.

(From the Department of Physics, Andhra University, Waltair.)

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1. Introduction.

The Raman spectrum of sodium nitrate has already been the subject of intensive investigation by a number of workers. Bär,[1] Krishnamurti,[2] Schæffer, Matossi and Aderhold,[3] Gerlach,[4] Nisi,[5] Cabannes and Canals,[6] Rao,[7] Ananthakrishnan[8] and others are among those that have studied the substance in the solid state. Some of these authors and certain others among whom mention may be made of Carelli, Pringsheim and Rosen,[9] Woodward[10] and Ramaswamy[11] have studied the stubstance in a dissolved state. Rao[7] has investigated the Raman spectrum of this substance in the fused state also. It is not necessary to review individually the work of each author here as there is general agreement on the essential points between the various workers. The main results will be briefly mentioned. The Raman frequencies obtained in the solid state are 103, 190, 730, 1074, 1391 and 1678. Of these 103 and 190 are regarded as lattice or external frequencies. 730, 1074 and 1391 are regarded as the three of the four possible fundamental frequencies of the NO_3 group ; the fourth one being represented by a strong, infra-red absorption at 830 but inactive in Raman scattering. 1678 is regarded as a combination frequency. In aqueous solutions one intense line at 1074 and two very weak lines at 730 and 1390 are obtained. The position of the line at 1074 in solutions is not exactly the same as that in the crystal and even in solutions it exhibits small shifts as the concentration is altered. This effect has been studied in great detail by Gerlach and others. The state of polarisation has been studied for only two lines, namely, 1070 and 720 and it has been observed that the former is strongly polarised whereas the latter exhibits almost complete depolarisation.

A careful review of the literature shows that most of the investigators cited above with the exception of Nisi, and Cabannes and Canals have only concerned themselves with studying the effect in powdered crystals. There

are certain disadvantages in this method such as the masking of some of the features relating to the lattice oscillations due to over-exposure of the central line. The author has thought it desirable to grow a large single crystal for the purpose of studying firstly the polarisation effects with special reference to crystal axes and secondly the lattice oscillations in greater detail laying special emphasis on the effect of temperature on these. This aspect of the subject does not seem to have received the attention of any of the authors cited above. No one studied the scattered light in the crystal at high temperatures, although certain authors such as Rao[7] have reported the results of a study of the substance in the molten state. In the present investigation, large, clear and well-formed single crystals have been grown and the lattice oscillations obtained with great clarity thus facilitating a study of the temperature effect on the same. Incidentally, very intense Raman spectra of sodium nitrate both in the solid and dissolved states have been obtained and described here.

2. *Raman Spectrum Obtained from a Large Single Crystal.*

A suitable single crystal was mounted in a closely fitting and dark enclosure and windows were provided for illumination and observation of scattered light. The scattered light was focussed by means of a Zeiss Biotar lens f/2·8, on to the slit of a two-prism glass spectrograph made by Adam Hilger, Ltd., London. An enlargement of the Raman spectrum obtained is reproduced in Plate VI. λ 4046 and λ 4358 are used as the exciting lines. It can be seen from the enlargement that it is quite free from continuous spectrum and that the lines due to the oscillations of both the nitrate ion and the lattice are recorded with great intensity. The lattice oscillations can be observed on both the Stokes and the Anti-Stokes sides of the exciting lines. Raman shifts as obtained in the present investigation are given in Table I along with those of a few other authors for comparison.

There are two possible models for the configuration of a group like AX_3. One is a pyramidal model and the other a plane model. It is now well established that the NO_3 and CO_3 groups come under the class of plane models. The normal modes of oscillation are six in number, two of which are single and two others doubly degenerate. In one of the former two, designated ω_2 in Table I, the nitrogen atom oscillates along the axis of symmetry and the resulting frequency is active in the infra-red but inactive in the Raman scattering. The reverse is the case with the second one in which the three oxygen atoms move out radially. This should occur strongly in Raman scattering but not at all in the infra-red absorption spectrum. The sharp

TABLE I.

Notation		Measurements				
Schæffer	Kohlrausch	Krishnamurti	Schæffer, Matossi Aderhold	Cabannes and Canals	Anantha-krishnan	Author
ν_0	ω_1	1066	1069·4	1074·2	1069	1069
ν_1	ω_3	1383·1	1385·6	1397·4	1385	1388
ν_2	ω_4	719·7	729·3	730·4	723	727
ν_3	ω_2					830
$2\nu_3$	$2\omega_2$		1665·4	1678·5		1669
ν_5			95	103·1		98
ν_6			185	190·1		186

and intense lines designated ω_1 is identical with this oscillation. ω_3 and ω_4 occurring at 1391 and 730 respectively represent the two doubly degenerate oscillations and arise from modes in which the atoms oscillate in the plane of the ion itself. Alternative assignments and explanations have been given in the literature (see I. R. Rao, reference No. 7) but they are obviously in error.

The explanation of the fourth frequency at 1669 in Raman effect has been somewhat obscure. It may not be a mere accident that 1669 is very nearly double the strong infra-red absorption at 830 and the coincidence suggests that 1669 is probably to be explained as an overtone of the strong infra-red absorption. If this explanation is accepted it has to be recognised that while the fundamental does not appear the overtone appears with a feeble intensity. This is at first somewhat curious but a closer consideration shows that in this particular model, the overtone of the mode under consideration has a better chance of appearing than the fundamental. Since in the mode designated ω_2 the nitrogen atom oscillates along the symmetry axis, it is easily seen that the polarisability ellipsoid is deformed with a frequency double that of the frequency of the molecule. The reason is that in this mode any particular configuration at an instant reaches its reflected configuration about the plane of the undisturbed configuration in half the period. It therefore follows that in the Raman spectrum of the nitrate ion if this

oscillation is at all to be represented, it should be represented only by the overtone and not by its fundamental.*

3. Effect of Temperature on the Raman Lines.

A specially constructed electric heater was made to surround the crystal. A mount of oxidised copper foil, prepared carefully so as to give a uniform dull black surface, is used for mounting the crystal and the rest of the experimental arrangements were substantially the same as those described in the earlier section. With such an arrangement the Raman spectra of the sodium nitrate crystal at low and high temperatures (280° C.) could be obtained side by side under exactly identical conditions.

Raman spectra thus obtained are reproduced in Plate VI.

The observed differences in the spectra are noted below :—

(i) There is a small shift of the main Raman line 1069 of the nitrate ion. The frequency at higher temperatures is about 3 to 4 wave-numbers smaller than that at the room temperature.

(ii) The lattice oscillations have undergone a profound change. In the cold substance the lattice oscillations are two, and as may be seen from the plate, the one at 185 is stronger than the one at 95. In the hot substance the frequency at 185 has almost disappeared and the frequency 95 has gained considerably in intensity. The effect may be seen more clearly in the original plate than in the reproduction. The observed differences suggest a release of the crystalline lattice forces in the heated state of the solid substance but do not seem to indicate the setting in of a free rotation of the nitrate ions.

4. Aqueous Solutions of Different Concentrations.

As has already been mentioned in the Introduction, some investigators have examined the effect of dissolving the nitrate in water on the principal frequencies of the nitrate group and certain interesting results have been reported. Information relating to the relative intensities of the various lines and the effect of dilution on the same does not appear to be available. The present section describes the results of a study of the Raman effect in aqueous solutions of sodium nitrate with special reference to the relative intensities of the various lines at different concentrations. It may be mentioned even at the outset that the lattice oscillations designated ν_5 and ν_6 in Table I, do not appear at all in the Raman spectra of aqueous solutions, as may be expected.

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* The above explanation has arisen out of a discussion with Mr. N. S. Nagendra Nath on the question of the appearance of the overtone to the exclusion of the fundamental frequency in the case of the carbonate and nitrate ions.

The Raman spectra of the substance were studied as before under identical conditions of illumination and scattering and the spectra photographed on the same plate using a Hartman Diaphram. The enlargements are reproduced in Plate VI. The pictures relate to (i) a single crystal, (ii) the concentrated solution from which the single crystal was grown, (iii) the concentrated solution diluted to double its volume. The following features may be noted in the picture.

(1) The principal frequency of the nitrate ion which has a value of 1069 in the crystal shifts in the solution and becomes somewhat smaller. With increasing dilution, the shift increases and the frequency becomes smaller and smaller. These effects are seen very clearly in the pictures reproduced in the plate.

The most recent work in this direction is that of Rao[7] who has studied the Raman frequencies of sodium nitrate in the solid, molten and dissolved states. Grassmann,[12] and Laird and Franklin[13] have also studied the aqueous solutions of sodium nitrate at various concentrations. Both these authors confirm the results of Gerlach. The results obtained in this investigation are in entire agreement with those reported by these authors.

(2) It is evident from the pictures that the line at 1400 is much stronger than the line at 730 in the single crystal whereas in the concentrated solution the line 730 has increased considerably in intensity while the line at 1400 has become comparatively feebler. Water bands have also appeared in the spectrum as may be expected. In dilute solution also the same features persist but the features are masked in the photograph on account of a continuous spectrum developing strongly in dilute solution. Cabannes and Canals[6] have made certain observations on the relative intensities of the various lines in the crystal and reported that of the two lines 730 and 1400 in the Raman effect on calcite and on sodium nitrate, the former is stronger in calcite and the latter in the nitrate.

The results obtained in the present investigation with the crystal of sodium nitrate confirm the observations of Cabannes and Canals and in addition they reveal certain interesting features. The relative intensities of the different modes of oscillation in Raman effect of the nitrate group undergo a change as the substance is dissolved in water, and in aqueous solutions the pattern resembles that of the carbonate ion in the solid state. It must be thus concluded that in the case of the nitrate ion in the solid state there are forces which restrict one mode of oscillation leaving another mode comparatively free but that these forces are released on dissolving the substance in water.

5. Summary.

The Raman spectrum of a large single crystal of sodium nitrate is obtained at the room temperature and at about 280° C. The frequency of the principal line at the high temperature is found to be about 3 to 4 wave-numbers smaller than that at the room temperature. Of the two lattice oscillations 185 and 95, the former is more intense at the room temperature whereas the latter is more intense at the high temperature.

The results obtained by the earlier workers in respect of solutions are confirmed. It is further reported that with increasing dilution, the frequency 730 gains considerably in intensity when compared with the frequency 1400. In this respect the nitrate ion solution resembles the carbonate ion in the solid state.

In conclusion, the author wishes to express his thanks to Mr. S. Bhagavantam for the facilities given to him and for his interest in the progress of the work.

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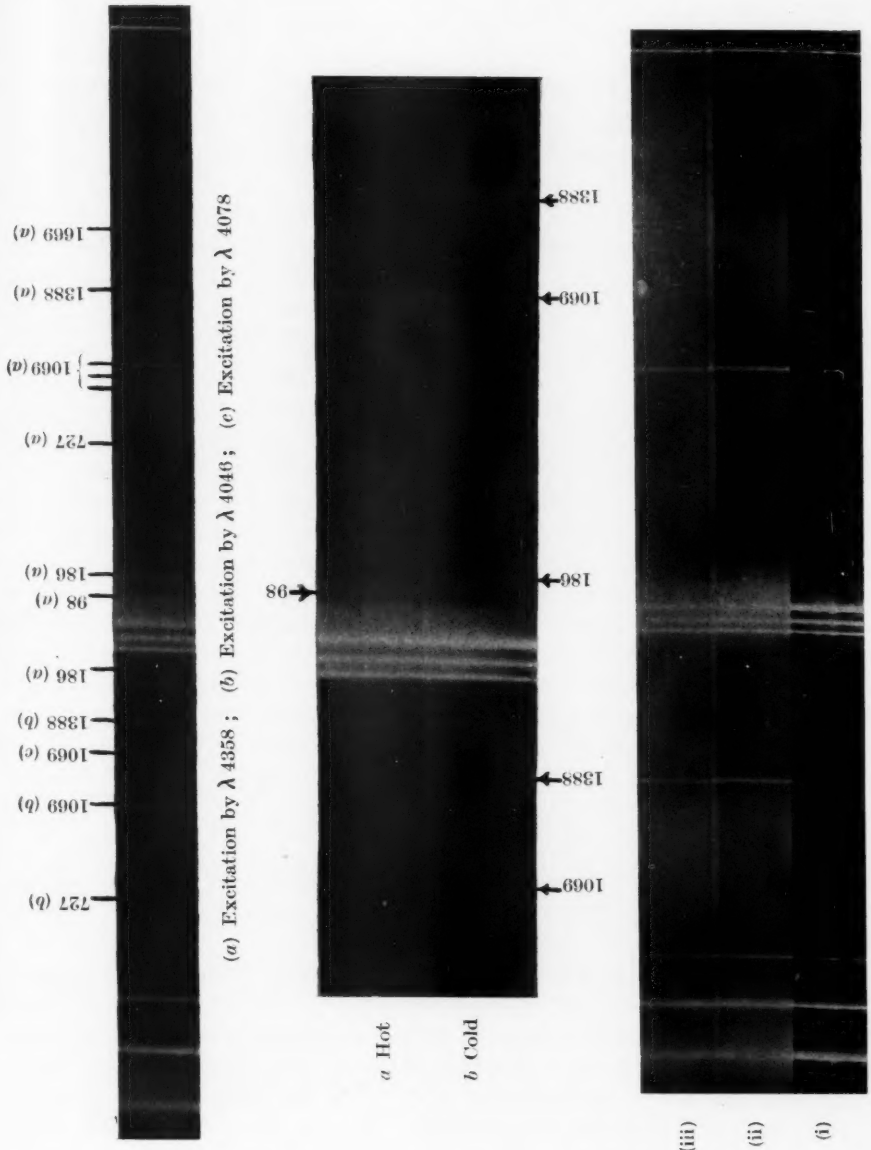
(a) Excitation by λ 4358 ; (b) Excitation by λ 4046 ; (c) Excitation by λ 4078
1669 (a)
1388 (a)
1069 (a)
727 (a)
186 (a)
98 (a)
186 (a)
1388 (b)
1069 (c)
1069 (b)
727 (b)
1388
1069
98
186
1388
1069
a Hot
b Cold
(iii)
(ii)
(i)

THE DISPERSION AND OPTICAL ANISOTROPY OF MOLECULAR OXYGEN IN RELATION TO ITS ABSORPTION SPECTRUM.

By P. Pattabhiramayya.

(From the Departments of Physics, Indian Institute of Science, Bangalore, and Andhra University, Waltair.)

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1. Introduction.

There are numerous determinations of the refraction of oxygen in the visible and near ultra-violet region and a list of references to such work are given by Stoll.[1] All these data except those of Koch[2] and Cuthbertson[3] and more recently those of Ladenburg and Wolfsohn[4] were used to determine the constants in a Cauchy dispersion formula with a view to the extrapolation of the value of the dielectric constant from the value of the refractivity for infinitely long waves. The three latter authors have however used formulæ of the Sellmier type and found certain fundamental frequencies of the molecule with which the dispersion in the region observed by them could be explained. None of these frequencies however seem to agree with the actually observed absorption frequencies of any considerable intensity in the extreme ultra-violet region to which they belong. A complete formula for dispersion based on the electron theory of matter may be written as

$$\mu^2 - 1 = \frac{Ne^2}{\pi mc^2} \Sigma \frac{f_n}{\nu_n^2 - \nu^2}. \qquad (1)$$

In the case of gases, this formula would become

$$\mu - 1 = \frac{Ne^2}{2\pi mc^2} \Sigma \frac{f_n}{\nu_n^2 - \nu^2}. \qquad (2)$$

This formula shows that the dispersion can be represented as a series where ν_n represents a number of absorption frequencies of the molecule and the constant f stands for the number of dispersion electrons in the classical, and the intensity of the vibrator in the quantum mechanical theory. Equation 2 has been used by Ladenburg and Wolfsohn in their paper.[4] As the data of the above authors are in an extended region from λ 5900 to λ 1920 they found that a single term formula would not fit in with their results and have therefore developed a two and a three-term formula to express their results. The corresponding dispersion constants are :

$\lambda_2 = 1468{\cdot}6$ Å with $f_2 = 0{\cdot}20238$, and
$\lambda_3 = 544{\cdot}36$ Å with $f_3 = 5{\cdot}9265$
in the two-term formula and
$\lambda_1 = 1898{\cdot}6$ Å with $f_1 = 4{\cdot}04 \times 10^{-5}$
$\lambda_2 = 1467{\cdot}9$ Å with $f_2 = 2{\cdot}0238 \times 10^{-1}$ and
$\lambda_3 = 544{\cdot}36$ Å with $f_3 = 5{\cdot}9276$
in the three-term formula.

None of the authors mentioned above seem to have considered the fact that the oxygen molecule is highly anisotropic optically. The purpose of the present paper is to take into account the anisotropic nature of the molecule in explaining the optical dispersion of oxygen.

2. Relation between Dispersion and Optical Anisotropy.

We may write the dispersion formula in the form

$$\mu^2 - 1 = \frac{Ne^2}{\pi mc^2} \sum_1^n \frac{f_{An}}{\nu_n^2 - \nu^2} + \frac{f_{Bn}}{\nu_n^2 - \nu^2} + \frac{f_{Cn}}{\nu_n^2 - \nu^2}, \tag{3}$$

in which it is assumed that the molecule has a series of characteristic frequencies and these have vibrator intensities of f_{A_1}, f_{A_2}, etc., f_{B_1}, f_{B_2}, etc., f_{C_1}, f_{C_2}, etc., respectively, along the three principal directions A, B, C of a molecule. The dielectric polarisability along a direction A will be proportional to $\sum_1^n \frac{f_{An}}{\nu_n^2 - \nu^2}$. The ratio of the polarisabilities along the three principal directions in a molecule will be

$$A : B : C = \sum_1^n \frac{f_{An}}{\nu_n^2 - \nu^2} : \sum_1^n \frac{f_{Bn}}{\nu_n^2 - \nu^2} : \sum_1^n \frac{f_{Cn}}{\nu_n^2 - \nu^2}.$$

If, however,

$$\frac{f_{A_1}}{f_{B_1}} = \frac{f_{A_2}}{f_{B_2}} = \ldots\ldots = \frac{f_{An}}{f_{Bn}} = k_1$$

and

$$\frac{f_{B_1}}{f_{C_1}} = \frac{f_{B_2}}{f_{C_2}} = \ldots\ldots = \frac{f_{Bn}}{f_{Cn}} = k_2.$$

Then the ratio A : B : C will be independent of ν and the anisotropy will show no dispersion and consequently the depolarisation of the light scattered by a molecule will be constant irrespective of the frequency of the incident beam. In every other case the optical anisotropy of the molecule will be a function of the frequency of the incident beam of light. Let us for the sake of argument take the case of a molecule having the three principal frequencies ν_1, ν_2, ν_3 and if we make the further assumption that $f_{A_1} = f_{B_2} = f_{C_3}$ and all the other f's zero, we get a dispersion formula of the type

$$\mu^2 - 1 = \frac{Ne^2 f}{\pi mc^2} \left[\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{\nu_2^2 - \nu^2} + \frac{1}{\nu_3^2 - \nu^2} \right]. \tag{4}$$

If further we assume that $\nu_2 = \nu_3$, (4) reduces to

$$\mu^2 - 1 = \frac{Ne^2f}{\pi mc^2}\left[\frac{1}{\nu_1^2 - \nu^2} + \frac{2}{\nu_2^2 - \nu^2}\right]. \tag{5}$$

What has been done above is equivalent to assuming that the same number of electrons contribute to the refractivity in all the three principal directions but with different natural frequencies. Expression (5) is appropriate to a diatomic molecule and implies that the electrons have a frequency of ν_1 along the axis and ν_2 in the plane of symmetry. In this particular case, the ratio of the principal polarisabilities A and C is given by

$$\frac{C}{A} = \frac{\nu_2^2 - \nu^2}{\nu_1^2 - \nu^2} \tag{6}$$

and varies in a simple manner with the frequency of the incident light.

When ν_1 and ν_2 are known the depolarisation of scattered light and its variation with the frequency of the incident light are easily calculated.

When the molecules are oriented at random as in a gas the average polarisability can be written as $\frac{C + 2A}{3}$ and if a denotes the ratio $\frac{A}{C}$, the degree of depolarisation ρ of ordinary light scattered by such an anisotropic molecule and observed perpendicular to the incident beam works out to be

$$\rho = \frac{2a^2 - 4a + 2}{4a^2 + 2a + 9}. \tag{7}$$

ρ will exhibit a dispersion since a depends upon the wave-length of the incident light.

To take account of the existence of absorption in regions other than the remote ultra-violet, we may write the dispersion formula for molecular oxygen in the form

$$\mu^2 - 1 = C_1\left\{\frac{1}{\nu_1^2 - \nu^2} + \frac{2}{\nu_2^2 - \nu^2}\right\} + \sum_{n=3}^{n=n}\frac{C_n}{\nu_n^2 - \nu^2}. \tag{8}$$

The terms under the summation are usually so small that their contribution to the anisotropy of the molecule, if any, may be neglected.

3. *The Absorption Spectrum of Oxygen Gas.*

The most important region of absorption is the system of bands observed by Hopfield[5,6] extending from λ 600 to λ 1000 and they are transitions from a triplet level to a possible triplet level or levels above 12·3 volts.[7] These bands were discovered during a study of the extreme ultra-violet spectrum of helium. In the intense continuous spectrum of molecular origin of helium the first absorption bands of O_2 and H_2 have been recorded. Only the

photographs have been reproduced and no measurements seem to have been published to date on oxygen. The picture shows two intense band systems in absorption and the centre of gravity of these systems have been read off roughly from the reproduction. They form the primary frequencies in the dispersion formula. The third band system which is of considerably lesser intensity is left out of account. These spectra were produced at a very low partial pressure of oxygen estimated by the author to be of the order of a few thousandths of a millimetre of mercury. From the ease with which they are produced it is legitimate to suppose that they are the most important bands representing the primary frequencies of the oxygen molecule.

The absorption bands that come next in importance are the Schumann-Runge bands observed and measured in absorption by Leifson.[8] These bands lie in the region λλ 1757–1971. His photographs show that in a cell of 25 cm. length and at a pressure of 240 mm. the bands just begin to appear and are very well developed at a pressure of 740 mm. These bands have been fully analysed and definitely classified as triplet-triplet bands. The bands usually appear in work with air-filled spectrographs in that region. These bands also should contribute a not inconsiderable amount to the refractivity of oxygen.

The weak Herzberg[9] absorption bands lie in the region λλ 2400–2600 and are developed in a column of 25 metres at a pressure of one atmosphere. Even these are found to have a small influence on the dispersion.

Lastly, there is the region of atmospheric absorption at λλ 5380–7710. This system of bands is not considered for the purposes of the present work.

There is also a region of continuous absorption below the region of Schumann-Runge bands and possibly below the region of Hopfield bands. The continuous absorption regions indicate the radiations that are potent in disrupting the molecule itself.

4. *The Dispersion Formula of Oxygen.*

The data used in the present work are those of Ladenburg and Wolfsohn.[4]

(*a*) *The Hopfield Bands.*—The formula representing the dispersion of oxygen and possessing the characteristics mentioned above is

$$\mu_\lambda^2 - 1 = 2{\cdot}7798\left[\frac{1}{1{\cdot}06281 \times 10^{10} - \nu^2} + \frac{2}{2{\cdot}07028 \times 10^{10} - \nu^2}\right]$$

or

$$= 2{\cdot}7798\left[\frac{1}{(0{\cdot}970)^{-2} \times 10^{-10} - \lambda^2} + \frac{2}{(0{\cdot}695)^{-2} \times 10^{-10} - \lambda^2}\right],$$

where ν and λ represent the wave-number and wave-length respectively of the incident light.

The primary frequencies found to represent the course of dispersion in the visible region are λλ 695 and 970. These are very strong absorption bands in the Hopfield bands and are by themselves sufficient to explain the dispersion from λ 5500 to λ 3500. *The degree of depolarisation, calculated with the help of expression* (6) *of section* 2 *is found to be* 6·68% *at* λ 5500 *in good agreement with the experimental result* 6·5% *for white light.*[10] *The formula also shows that the depolarisation at* λ 2500 *should increase to* 9·73%. The extent of the agreement of the course of dispersion on the basis of these considerations is given in Table I.

TABLE I.

λ	$(\mu - 1) \times 10^4$		
	Obs.	Cal.	Obs. — Cal.
5500	2·7136	2·7142	0·0006
5000	2·7282	2·7281	0·0001
4500	2·7467	2·7470	— 0·0003
4000	2·7750	2·7738	— 0·0012
3500	2·8196	2·8149	— 0·0047
3000	2·8914	2·8792	— 0·0122
2500	3·0362	2·9947	— 0·0415
2000	3·4406	3·2371	— 0·2035

It is evident from this table that the formula is applicable to the visible region and expresses the results quite satisfactorily to within the limits of experimental error. It first begins to fall at about λ 3500 and the nature of the systematic error indicates quite clearly that the influence of another absorption region must be introduced to express the experimental course of the dispersion.

(*b*) *Schumann Bands.*—The next region of absorption to be taken into consideration is the Schumann bands λλ 1757 to 1925 and the region of continuous absorption further down to λ 1300. An attempt will be made in this paper to show that the course of the dispersion of oxygen can be explained by taking into consideration only band absorption. It appears from the

results that continuous absorption has no influence on the dispersion of the gas. Considering then, that a part of the dispersion is explained by the formula already proposed, it is sought to explain the remaining part of it by taking a representative band in the Schumann region. It is found that the band at λ 1831 represents to a very large extent the influence of the band system and its influence is shown in Table II.

TABLE II.

$\lambda_1 = 970$; $\lambda_2 = 695$; $C_1 = C_2 = 2{\cdot}7304$; $\lambda_3 = 1831$; $C_3 = 0{\cdot}0252$.

λ	$(\mu - 1) \times 10^6$				
	Obs.	Cal.			Obs. — Cal.
		970 and 695	1831	Total	
5500	2·7136	2·6660	·0475	2·7135	0·0001
5000	2·7282	2·6796	·0488	2·7284	— 0·0002
4500	2·7467	2·6982	·0506	2·7488	— 0·0021
4000	2·7750	2·7245	·0532	2·7777	— 0·0027
3500	2·8196	2·7644	·0581	2·8225	— 0·0029
3000	2·8914	2·8280	·0673	2·8953	— 0·0049
2500	3·0362	2·9414	·0912	3·0326	0·0036
2000	3·4406	3·1796	·2610	3·4406	0·0000

In Table II the influence on refraction of the primary frequencies and the subsidiary frequency have been shown separately.

(*c*) *Herzberg Bands.*—A glance at the last column will show that about λ 2500 there is a sudden change in the sign of the error indicating the influence of another absorption region. We now introduce a frequency taken from the Herzberg band region to express the course of dispersion. Table III will show the entire course of dispersion between λλ 5500–2000. The representative frequency in the Schumann band system is slightly shifted (λ 1847)

and λ 2429 is taken to represent the Herzberg band system and the agreement between calculated and observed values is as good as can be expected. The table also shows the contribution of each frequency to the refraction and the value of the corresponding constant.

TABLE III.

	$(\mu - 1) \times 10^{-4}$					
		Calculated				
λ	Obs.	C = 2·7331	C = 0·0223	C = 0·000137	Total	Obs. − Cal.
		970,695	1847	2429		
5500	2·7136	2·6687	0·0428	0·0005	2·7120	0·0016
5000	2·7282	2·6822	0·0440	0·0006	2·7268	0·0014
4500	2·7467	2·7008	0·0457	0·0006	2·7471	−0·0004
4000	2·7750	2·7272	0·0483	0·0007	2·7762	−0·0012
3500	2·8196	2·7671	0·0527	0·0008	2·8206	−0·0010
3000	2·8914	2·8308	0·0612	0·0012	2·8932	−0·0018
2500	3·0362	2·9444	0·0837	0·0073	3·0354	0·0008
2000	3·4406	3·1827	0·2585	$\overline{0·0008}$	3·4404	0·0002

The bar indicates that the contribution is negative.

(*d*) *Band Structure.*—To obtain a reasonable fit in the entire range of the observations down to λ 1920 which lies in a region of absorption bands, a series of suitable frequencies will have to be taken in order to represent the effect of the several bands in that region. Table IV gives a scheme of frequencies which can be used to explain the dispersion within limits of experimental error.

TABLE IV.

Contributions to Refractivity					Refractivity $(\mu^2-1).10^4$	λ	Refractive Index $(\mu-1)\times 10^4$		
λ 970 ; 695	1831	1903	1971	2429			Obs.	Cal.	Obs. – Cal.
C 2·7411	0·0168	0·0004	0·0010	0·0003					
5·3528	0·0634	0·0016	0·0045	0·0022	5·4245	5500	2·7136	2·7122	0·0014
5·3802	0·0651	0·0017	0·0046	0·0023	5·4539	5000	2·7282	2·7270	0·0012
5·4175	0·0676	0·0017	0·0048	0·0025	5·4941	4500	2·7467	2·7470	−0·0003
5·4704	0·0710	0·0019	0·0054	0·0028	5·5515	4000	2·7750	2·7757	−0·0007
5·5505	0·0776	0·0021	0·0058	0·0034	5·6394	3500	2·8196	2·8197	−0·0001
5·6782	0·0897	0·0024	0·0068	0·0051	5·7822	3000	2·8914	2·8911	0·0003
5·9060	0·1216	0·0035	0·0103	0·0317	6·0731	2500	3·0362	3·0366	−0·0004
6·3840	0·3485	0·0153	0·1350	$0\cdot\overline{0037}$	6·6791	2000	3·4406	3·4396	0·0010
6·5104	0·6230	0·0821	$0\cdot\overline{0383}$	$0\cdot\overline{0029}$	7·1743	1920	3·5887	3·5871	0·0016

The bars on the figures indicate negative contributions.

The work shows that finer and finer fit could be achieved by increasing the number of representative frequencies in an absorption region and by suitably adjusting the small constants which occur with the subsidiary frequencies so as to represent the intensity of the individual bands chosen. Even the band system of atmospheric oxygen at λλ 5380–7710 could be taken account of. It is thus seen that the dispersion can be expressed exclusively in terms of the actually observed band systems in the case of oxygen. It is not necessary to invoke the assistance of purely hypothetical frequencies though the number of such frequencies chosen is small.

5. *Significance of the Constants in the Formula.*

The value of the constants in the formula may be interpreted in terms of the *f*-numbers due to Ladenburg and at the same time can be used to determine the number of dispersion electrons according to the Drude theory. The constant in Equation 8 which represents the dispersion sufficiently well in the visible region gives the number of dispersion electrons as 3·5, whereas the number of such dispersion electrons calculated from the value of the constant associated with the wave-length λ 544 in the formula of Ladenburg and Wolfsohn would give an utterly disproportionate number.

Interpreting them in terms of the *f*-numbers they show how the vibrator intensity is very high in the extreme ultra-violet such that the frequencies in the extreme ultra-violet are responsible for accounting for a large bulk of the refractivity of the gas. All the same the subsidiary frequencies have their own influence on the refractivity. These vibrator frequencies are also indicative of the fact of the widely different pressures at which the various absorption spectra are developed. Whereas the Hopfield absorption bands are developed at pressure of the order of a few thousandths of a mm. of mercury, the Schumann absorption bands just show up only at a pressure of 240 mm. in a column one metre long and become very marked at a pressure of 740 mm. The weak absorption bands observed by Herzberg show up in a column of 25 metres length at atmospheric pressure. These facts are in qualitative agreement with the values of the three constants associated with the three frequencies given in Table III. The values are 2·73 for the Hopfield bands, $2{\cdot}23 \times 10^{-2}$ for the Schumann bands and $1{\cdot}37 \times 10^{-4}$ for the Herzberg bands. The new formula proposed for the dispersion of oxygen has thus constants which have a meaning both on the classical as well as on the quantum mechanical theory of dispersion. Moreover it satisfactorily accounts for the optical anisotropy of the molecule. Besides this, the theory predicts an appreciable increase of the optical anisotropy in the ultra-violet region for the oxygen molecule. Experimental evidence available in this direction is very meagre and conflicting views regarding the dispersion of depolarisation in scattered light are expressed in the literature connected with the scattering in liquids.[11] An experimental study of the phenomenon is evidently of great importance in relation to the theory of dispersion and only preliminary experiments with oxygen were carried out by the author which indicated qualitatively a dispersion in the expected direction.

6. *Summary.*

A new dispersion formula for gaseous oxygen has been worked out, which is simultaneously able to explain the observed optical anisotropy of the oxygen molecule and its dispersion. The characteristic frequencies found are λ 695 and λ 970 in the Hopfield absorption band region, λ 1831, λ 1903 and λ 1971 in the Schumann region and λ 2429 in the region of the Herzberg bands. The two frequencies found in the Hopfield band region are alone sufficient to explain the dispersion between λλ 5500 to 3500 and give depolarisation of scattered light of 6·68% at λ 5500 in good agreement with the observed depolarisation of 6·5% using white light. The frequencies used to explain the dispersion are all from these of actually observed absorption bands in the spectrum of the oxygen molecule. In no case is it necessary

to choose any frequencies from the regions of continuous absorption. The constant associated with the frequencies λ 695 and λ 970, *viz.*, 2·7798 yields a value of the number of the dispersion electrons of 3·5 while the *f*-numbers associated with $\lambda\lambda$ 695 and 970, λ 1847 and λ 2429, *viz.*, 2·7332, $2 \cdot 23 \times 10^{-2}$ and $1 \cdot 4 \times 10^{-4}$ respectively are in consonance with the vibrator intensities which explain the relative case with which the various absorption bands can be developed.

In conclusion, the author wishes to express his thanks to Prof. Sir C. V. Raman under whose suggestion and guidance this work was carried out during his stay at the Indian Institute of Science, Bangalore, and to Mr. S. Bhagavantam for his interest in the work.

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SPECIFIC HEATS OF LIQUIDS IN RELATION TO RAMAN EFFECT DATA.

By S. Bhagavantam.

(From the Department of Physics, Andhra University, Waltair.)

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1. Introduction.

Since the discovery of the Raman effect, various attempts have been made to utilise the observed Raman frequencies for the purpose of explaining the specific heats of substances. Mention may be made here of the work of Andrews and Southard (1930), Bhagavantam (1930) and Paramasivan (1931). The subject may be broadly divided into two distinct parts ; one relating to the specific heats at low temperatures and the other to the specific heats at the room temperatures. In the former case, the major part of the specific heat is explained with the help of the Debye theory and the investigation should therefore proceed on the lines of ascertaining the exact relationship, if any, between the Debye elastic spectrum and the low frequency oscillations recorded in the Raman scattering by solids. On the other hand, at comparatively higher temperatures all Debye functions based on low frequencies reach their limiting values and therefore the exact frequencies on which they are based are not of much significance. The contribution from internal frequencies, however, becomes appreciable at these temperatures and a full knowledge of these is therefore necessary to predict the specific heat and its variation with temperature. The present paper deals with this latter aspect and the specific heats for benzene, carbon tetrachloride and carbon disulphide are calculated at several temperatures in the neighbourhood of the room temperature. These liquids have been chosen as their internal frequencies are now reliably known. Certain interesting conclusions are arrived at by considering the results of such calculations and these are set forth here.

2. Choice of Debye Limits and Internal Frequencies.

Lord, Ahlberg and Andrews (1937) have recently satisfactorily explained the specific heat data in respect of solid benzene at low temperatures by assuming a mean characteristic temperature $\theta = 150$ to represent the contribution of the benzene lattice to the specific heat. The three degrees of

translational freedom are taken to give rise to compressional waves and the three degrees of rotational freedom are taken to give rise to torsional waves and these waves are assumed to take up energy in the manner described by the Debye function. The contribution to specific heat on account of these six degrees of freedom will then be $6RD\left(\frac{\theta}{T}\right)$ at T. The exact relationship between the Debye limit corresponding to $\theta = 150$ and the observed low frequency Raman lines in solid benzene has not been discussed by these authors. They even seem to be of the opinion that there is no justification for expecting such a relationship to exist (Blackman, 1935). The internal frequencies of the benzene molecule have been given by Lord and Andrews (1937) after a careful consideration of the Raman effect and infra-red data as 406 (2), 538 (1), 606·4 (2), 670 (1), 849·7 (2), 992·6 (1), 1008 (1), 1025 (2), 1145 (1), 1160 (2), 1176·0 (2), 1190 (1), 1477 (2), 1520 (1), 1595 (2), 1854 (1), 3048·3 (2), 3061·5 (1), 3063 (1), 3077 (2). The number in the bracket in each case represents the degeneracy of the corresponding oscillation and the total number of degrees of freedom comes out as 30 as it ought to. To each of these is assigned an Einstein function, and the aggregate specific heat is calculated. The good agreement obtained by these authors in the entire range in which they have investigated (0 to 270° K.) is convincing proof of the fact that the choice of the fundamental frequencies has been correctly made. We may therefore write down equations (1) and (2) to represent respectively the specific heats of solid and vapour benzene :

$$C_v = 6RD\left(\frac{\theta}{T}\right) + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{KT}\right) \qquad (1)$$

$$C_v = 3R + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{KT}\right) \qquad (2)$$

θ in equation 1 is equal to 150.

In the case of vapour, each of the three translational and three rotational degrees of freedom has assigned to it a mean energy of $\frac{KT}{2}$ per molecule. In the case of a liquid, we do not know whether (1) or (2) will be applicable and hence we will examine both these equations.

In the case of CS_2 and CCl_4, we will assume similar equations. As has already been mentioned, the exact value of θ is not very important as for all low values which are ordinarily met with in such cases, the Debye function nearly reaches its limit at the room temperature. Thus the first term of (1) may be put equal to 12 calories in CCl_4. In CS_2, it should, however, be taken as 10 calories as out of a total of 9 degrees of freedom, only 5 are taken

over by the lattice, the other 4 being internal. The vibrational frequencies and their degeneracies in each case are given below :

CCl_4 : 217 (3), 313 (2), 459 (1), 777 (3)

CS_2 : 397 (2), 655 (1), 1523 (1).

3. Results.

TABLE I.

Specific Heat of Liquid Benzene at Constant Volume.

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Mills and McRae)	Observed (Williams and Daniels)
0	11·72	9·68	21·40	15·68	21·15	..
20	11·76	11·01	22·77	17·01	22·09	21·57
40	11·78	12·44	24·22	18·44	23·00	23·13
60	11·80	13·83	25·63	19·83	24·06	25·22
90 (vapour)	..	16·0	..	22·0	23·4*	..

* Observed C_p is taken from *I.C.T.* and C_v obtained therefrom by subtracting 2 calories.

TABLE II.

Specific Heat of Liquid CCl_4 at Constant Volume.

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Mills and McRae and Williams and Daniels)
0	12	11·53	23·53	17·53	21·24
20	,,	12·05	24·05	18·05	21·50
40	,,	12·52	24·52	18·52	21·69
60	,,	12·94	24·94	18·94	22·41
80	,,	13·32	25·32	19·32	22·82

TABLE III.

Specific Heat of Liquid CS_2 at Constant Volume.

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed (Regnault)
0	10	3·64	13·64	8·64	11·70
20	,,	3·89	13·89	8·89	11·70
40	,,	4·12	14·12	9·12	11·77
97 (vapour)	..	4·66	..	9·66	9·95†

† C_p is taken from *I.C.T.* and C_v obtained therefrom by subtracting 2 calories.

In the above tables, the observed values of C_v for benzene are obtained from the work of Mills and McRae (1910) and Williams and Daniels (1924). These authors have given C_p at different temperatures and C_v is calculated therefrom by reducing it in the ratio of the adiabatic and isothermal compressibilities as determined by Tyrer (1913). The results of Mills and McRae at higher temperatures are consistently lower than those obtained by Williams and Daniels and the differences in the case of benzene are appreciable. The data of both authors are given in Table I. The results of the latter authors however appear to be more reliable at high temperatures. In the case of CCl_4, the differences are not so prominent and at the two lower temperatures (0 and 20) the values of Mills and McRae and at all the other temperatures those of Williams and Daniels are given. In the case of CS_2, results of very early work of Regnault are the only ones available and these are given. In both these cases also C_v is calculated from the observed C_p in the manner described above. C_p for the vapours of benzene and CS_2 is available and C_v is obtained therefrom and given in Tables I and III. No reliable value for the specific heat of CCl_4 vapour is available.

4. *Discussion of Results.*

The following features may first be noted:

1. The agreement between the calculated and the observed specific heats is very satisfactory in the case of benzene and CS_2 vapours.

2. The specific heat observed in the vapour state is less than that obtained in the liquid.

3. In all the three cases, the observed specific heats for the liquid state at all temperatures lie between those calculated on the one hand by treating the liquid as a solid and on the other by treating it as a gas.

4. In the case of benzene the observed values are much closer to the solid values than in the other two cases where they are midway between the two sets of calculated values.

These results may be interpreted as follows :—

The thermal motion of liquid molecules which goes to make up its heat content is neither wholly disorganised in the form of random movements as in a gas nor wholly organised in the form of elastic waves as in the case of a solid. This important conclusion emerging out of the present investigation is not entirely new but has already been indicated recently from other branches of work mainly in light scattering. Particular attention may be drawn to the work of Raghavendra Rao (1935) on the fine structure of Rayleigh scattering. The presence of two displaced Brillouin components in the light scattered by liquids can only be explained by assuming that part of the thermal movements in the liquid are in an organised form constituting high frequency sound waves and causing the shift in the scattered light. On the other hand, the presence also of a central undisplaced component is to be associated with the fluctuations in density caused by the random movements of the molecules. Quantitative data regarding the relative intensities of these components are not available but a significant observation of Raghavendra Rao that the central component in CCl_4 is unusually bright in relation to the outer components when compared to the other cases such as benzene and toluene, may be cited here. It is particularly gratifying that the same result is arrived at from a study of the specific heats of liquids, a branch which is directly concerned with the manner in which heat energy is taken up by the molecules. It cannot be a mere accident that the observed specific heat of benzene liquid at various temperatures is quite close to that calculated on the assumption that the entire translational and rotational thermal energy is in the form of elastic waves whereas in the case of CCl_4 the observed value is well below the value so calculated and is as near to the gas value as to that of the solid. A good portion of the thermal energy is therefore taken up by a disorganised movement of the CCl_4 molecules in the liquid and hence we should expect a relatively strong, central or undisplaced scattering.

A quantitative investigation of the relative intensities of these components in relation to the observed specific heats is likely to throw considerable light both on the theories of specific heats as applied to liquids and nature

of the liquid state. Recent work of Raman and Raghavendra Rao (1937) on the viscous liquids is of great significance in this respect and the variation of specific heats of such liquids with temperature is likely to reveal irterest-ing facts. Reliable data are, however, not available in these cases but work is in progress in this laboratory. There is also the additional difficulty of uniquely fixing the fundamental frequencies in such cases but by choosing substances for which complete Raman effect data are available, some progress may be expected.

5. Summary.

The specific heats of liquid benzene, CCl_4 and CS_2 are calculated with the help of the known fundamental frequencies in each case at different temperatures. Two alternative methods of evaluating the contribution to specific heat of translational and rorational degrees of freedom are adopted. In the first, a Debye function is assumed as in the case of a solid and in the second, a mean energy of $\frac{KT}{2}$ per degree of freedom per molecule is assigned as in the case of a gas. The observed specific heats are found to lie between these two extremes. It is therefore concluded that in liquids thermal movements of molecules are partly in an organised manner constituting Debye elastic waves as in a solid and partly in a random manner as in a gas. Analogy is drawn between this conclusion and the results obtained in light-scattering in respect of the fine structure of the Rayleigh line in liquids where two displaced Brillouin components and one undisplaced central component are usually observed.

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THE RAMAN SPECTRUM AND CONSTITUTION OF PENTAERYTHRITOL.

By P. G. N. Nayar.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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1. Introduction.

The structure of pentaerythritol C $(CH_2OH)_4$ has been the subject of a great deal of discussion in recent years, in view of the supposed possibility of a pyramidal structure for the molecule. Mark and Weissenberg (1923) who first carried out the X-ray analysis of pentaerythritol came to the conclusion that four carbon atoms are situated at the corners of the base of a square pyramid, with the fifth carbon atom at its apex. This has been later supported by Huggins and Hendricks (1926). This result has been cited in support of the view held by Guillemin (1926) and Henri (1927) that molecules of the type CA_4, in particular methane (CH_4), have a pyramidal structure. Dipole moment measurement of pentaerythritol (Sidgwick, 1933) shows a large moment (about 2) which has been ascribed to the association of the hydroxyl groups; but the tetrachloride and tetrabromide of pentaerythritol, which possess attached unsymmetrical groups, show a zero moment. From these results it is difficult to conclude in favour of either a pyramidal or tetrahedral structure.

A square pyramidal structure as suggested above is untenable stereochemically. Later investigations on the crystal structure of pentaerythritol and its derivatives go to show that the earlier crystal structure measurements are incorrect. Very recently Nitta (1937) and Llewellyn, Cox and Goodwin (1937) have carried out quantitative X-ray measurements and determined the complete structure of the pentaerythritol molecule. Their finding is that the central carbon atom is surrounded tetrahedrally by four methylenic carbon atoms, and the deviation of the bond angle from the true tetrahedral value of $109\frac{1}{2}°$ is negligible.

The Raman spectrum of this substance has not been studied so far and it would be of interest to see what light it can throw upon the structure of the molecule.

2. *Experimental Arrangements and Results.*

The substance used was from Kahlbaum's stock of pure chemicals and was available in the form of coarse transparent crystals. The spectrum was taken on a Zeiss 3-prism glass spectrograph with a dispersion of about 20 Å. U. per mm. in the λ 4047 region. The technique of complementary filters devised by Ananthakrishnan (1937) for crystal powders was employed. The λ 4047 mercury line, isolated from higher wave-lengths by a solution of iodine in carbon tetrachloride, was used for excitation, and this line was weakened before the scattered light entered the spectrograph by a very dilute solution of sodium nitrite which however allowed the low frequency lines to be recorded. An intense picture was obtained with a five days exposure. The Raman spectrum is reproduced in the accompanying plate and the frequencies are tabulated in Table I, with visual estimates of relative intensities. The letters *s*, *b*, *d* signify respectively sharp, broad and diffuse character of the lines.

TABLE I.

Raman Frequencies of Pentaerythritol $[C\ (CH_2OH)_4]$.

Exciting line $\lambda = 4047$ Å.U. $\nu = 24705$.

No.	ν	$\Delta\nu$ in cm.$^{-1}$	Intensity	
1	24262	443	2*d*	
2	24195	510	1*d*	
3	23894	811*	6*s*	
4	23831	874	5*s*	
5	(23696)	(1009)	0	Doubtful
6	23668	1037	3*s*	
7	23631	1074	6*s*	
8	23575	1130	2*d*	
9	23484	1221	0	
10	23473	1232	5*b*	
11	23424	1281	2*b*	

TABLE I—(*contd.*)

No.	ν	$\Delta\nu$ in cm.$^{-1}$	Intensity	
12	23309	1396	2*b*	
13	23271	1434	3*b*	
14	23228	1474	4*b*	
15	21962	2743	3*b*	
16	21871	2834	2*b*	
17	21821	2884	0	
18	21782	2923*	9*b*	
19	21771	2934	4	Not well resolved
20	21744	2961*	10	Band of about 35 wave-numbers.
21	21453 21370	3252 3335 } †	2	

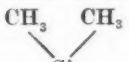
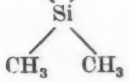
* Indicates that these lines have corresponding 4077 excitation also.
† A diffuse band extending over 170 wave-numbers, with a doublet structure.

3. *Discussion.*

The total number of atoms in the pentaerythritol C $(CH_2OH)_4$ molecule is twenty-one and for such a molecule, fifty-seven normal modes of vibration are possible. If the molecule were tetrahedral, it would have a centre of symmetry and some of these frequencies would be degenerate or forbidden in the Raman effect. In general, the number of Raman lines excited in this case would be less than half the total number of normal modes of vibration. For a lower order of symmetry, as in the pyramidal structure, the number of vibrations would be generally more than twenty-eight and less than fifty-seven. In the present case, the author has obtained a very intense picture for the substance and it may reasonably be taken as its complete Raman spectrum. The total number of lines recorded is twenty-one. Even excluding the possibility of a few of these being due to overtones or combinations, the observed number of lines is less than twenty-eight. This result indicates a tetrahedral structure, not only for the inner carbon core, otherwise called the "neopentyl group," but also for the molecule as a whole, in agreement with the X-ray evidence.

Taking only the carbon atoms into account, the molecule is of the type AX_4 with tetrahedral symmetry. A molecule of this type has four fundamental frequencies ν_1, ν_2, ν_3 and ν_4, of which ν_1 is single and symmetrical, ν_2 is doubly degenerate, and ν_3 and ν_4 are triply degenerate (Kohlrausch, 1931). All four are active in the Raman effect. Rank and Bordner (1935) have studied a number of molecules of a similar type, namely, silicon tetramethyl Si $(CH_3)_4$, tetramethyl methane C $(CH_3)_4$ and a number of substitution products of the latter. They have classified the spectra of tetramethyl methane and its derivatives in relation to the tetrahedral structure of the " neopentyl group ", and assigned a sharp and intense line at 733 cm.$^{-1}$ to the " breathing frequency " of the " neopentyl group ". This frequency has also been observed in camphoric acid and camphoric anhydride in which the " neopentyl group " is present, by Singh and Misra (1937) at 705 cm.$^{-1}$ and 607 cm.$^{-1}$ In pentaerythritol the corresponding frequency appears at 811 cm.$^{-1}$ The frequencies reported by Rank and Bordner (*ibid.*) for silicon tetramethyl and tetramethyl methane and the author's results for pentaerythritol are given in Table II. Frequencies above 1500 cm.$^{-1}$ have been omitted.

TABLE II.

Substance	Raman frequencies in cm.$^{-1}$ with intensities
	202 (10*b*), 239 (8 *b*), 598 (10 *s*), 696 (8 *b*), 863 (5 *b*), 1264 (5 *b*), 1427 (8 *b*)
	335 (5), 414 (2), 733 (10), 925 (8 *b*), 1252 (10 *b*), 1455 (8 *b*)
	443 (2 *d*), 510 (1 *d*), 811 (6 *s*), 874 (5 *s*), 1009 (0), 1037 (3 *s*), 1074 (6 *s*), 1130 (2 *d*), 1221 (0), 1232 (5 *b*), 1281 (2 *b*), 1396 (2 *b*), 1434 (3 *b*)

It can be seen that corresponding to the two lowest frequencies 202 cm.$^{-1}$ and 239 cm.$^{-1}$ in silicon tetramethyl, and 335 cm.$^{-1}$ and 414 cm.$^{-1}$ in tetramethyl methane, there are two low frequency lines at 443 cm.$^{-1}$ and 510 cm.$^{-1}$ in pentaerythritol. These lines are to be assigned to ν_2 and ν_4 as in the case

of the above substances, and they are diffuse as is to be expected from the degenerate nature of these vibrations. The diffuse line at 1130 cm.$^{-1}$ should similarly be assigned to ν_3.

Pentaerythritol is an aliphatic alcohol and we may expect some similarity between its spectrum and that of other aliphatic alcohols. The frequencies of methyl and ethyl alcohols are represented schematically in Plate VII. The values for the alcohols are taken from the *Landolt Börnstein* Tables (1935). The corresponding lines are joined together by dotted lines. It may be seen from the figure that for almost all lines below 1500 cm.$^{-1}$ with the exception of the four frequencies attributed to the " neopentyl group " in the earlier part of the discussion, there are corresponding Raman lines in the methyl and ethyl alcohols. In the region above 2700 cm.$^{-1}$ pentaerythritol has a greater number of lines than in the alcohols and this is obviously due to the fact that there are four CH_2OH groups placed at the corners of a tetrahedron in pentaerythritol in place of one such group in the latter.

The X-ray studies mentioned above have revealed that the molecules in the crystal lattice of pentaerythritol are linked together by " hydrogen bridges ". Venkateswaran (1938) has shown that the frequency characteristic of O–H in the Raman spectrum, where the hydroxyl group is involved in a " hydrogen bond ", is considerably lowered from its normal value in the free hydroxyl group and becomes diffuse. The O–H band in pentaerythritol is similar to that reported by Venkateswaran in strong acids and its frequency is about 3252 cm.$^{-1}$ and 3335 cm.$^{-1}$ From this we are led to conclude that the molecules in the substance are linked together by " hydrogen bonds ". The doubling of the O–H band is characteristic and a similar doubling has been reported in ethyl alcohol.

In conclusion, my grateful thanks are due to Professor Sir C. V. Raman for his kind interest and encouragement in the work. My thanks are also due to Dr. C. S. Venkateswaran for helpful suggestions.

4. *Summary.*

The Raman spectrum of pentaerythritol has been studied in the solid state and twenty-one frequencies observed. The molecule has been shown to possess tetrahedral symmetry in agreement with recent X-ray studies, and the frequencies have been discussed with reference to the " neopentyl group " and the frequencies in other aliphatic alcohols. The O–H frequency has been found to be characteristic of the presence in the crystal of the linking of molecules by the " hydrogen bond ".

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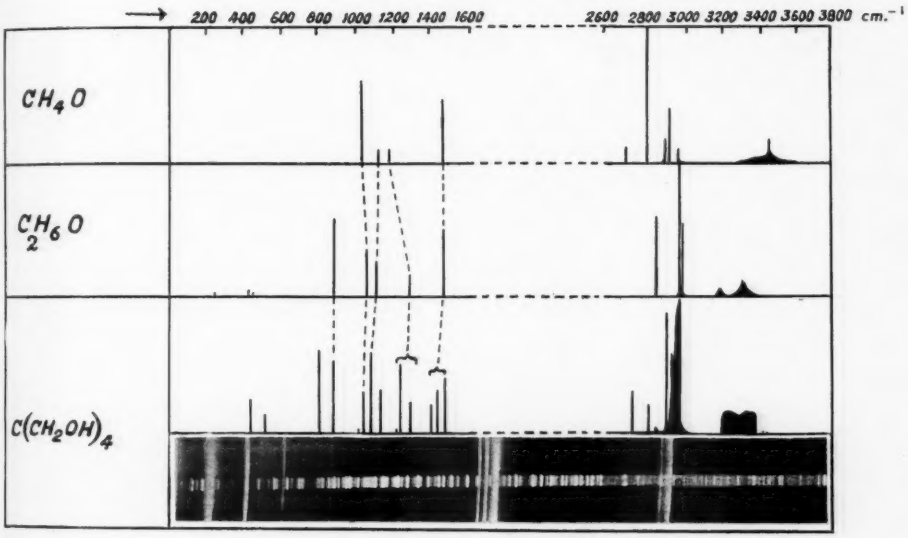
200 400 600 800 1000 1200 1400 1600
2600 2800 3000 3200 3400 3600 3800 cm.⁻¹
CH_4O
C_2H_6O
$C(CH_2OH)_4$